SECOND YEAR COLLEGE CHEMISTRY

A Manual of Laboratory Exercises

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PREFACE

THE work outlined in this manual is intended to accompany the author's text, "Second Year College Chemistry." It may, according to the author's experience, be used in connection with a course in quantitative analysis. The general order of procedure in both classroom and laboratory has been outlined in the preface to the text.

All the experiments here presented have been carefully tested out with several classes of students and then carefully rewritten. The author feels, therefore, that careful following of directions will insure good results. In all work of a quantitative nature, however, neatness and natural aptitude are prime factors which cannot be forced upon the student. The student who is naturally sloppy and clumsy will probably emerge from any course with his original traits, and will never measure up as a real chemist. However, neatness and skill on the part of the teacher are also necessary, for even a good student may be ruined by lax supervision and a careless example.

The apparatus employed in the experiments is made as simple as possible. This has been done for two reasons: first, the author desires to make it possible to work through this entire manual in places where the cost of more elaborate apparatus would be prohibitive; and second, he desires to emphasize principles rather than the bewildering details of refined methods and instruments. On the other hand, the aim has been constantly kept in mind to make the work accurate and truly quantitative. Careful directions have been included for the preparation of all the apparatus, although this preparatory work need not always be done by the student where the time is limited.

One of the most important parts of successful laboratory work is the careful keeping of a notebook. The teacher is, therefore, urged to insist that neat, accurate notes accompany each experiment. These notes should be taken *in the permanent notebook* and *in their final form, as soon as the data are obtained.* The habit of writing notes on scraps of paper and afterwards copying them off in " better form " is pernicious. Proper entry of notes should be regarded as part of every experiment, not a separate exercise. *Whether or not an experiment is going to suc-*

ceed has no bearing on the recording of the notes, for the notes on a failing experiment may be more valuable than those on a successful one.

The teacher's attention is called to the Appendix of this manual, where suggestions are given regarding the organization of the laboratory work, and regarding apparatus, chemicals, etc. These suggestions are intended simply to give the teacher who is just taking up the course the benefit of the author's experience, and thus considerably lighten the burden.

W. H. C.

OBERLIN, OHIO,
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TABLE OF CONTENTS

APPENDICES

LABORATORY MANUAL

CHAPTER I

KINETIC THEORY

Exp. 1. Brownian Movement.

Apparatus.—A compound microscope, a slide and a cover glass.

Procedure.—Take about 0.01 gm. (do not weigh) of gum gamboge, and rub in the palm of the hand with a drop or two of water to a smooth paste. Dilute somewhat, place a drop of the suspension on the slide and then put the cover glass in place. With a $10\times$ eyepiece and a 4 mm. objective, there will be no difficulty in seeing that some of the more or less isolated particles are in rapid vibration.

You should apply to the instructor for directions in using the instrument. Be very careful in any case not to turn the objective down against the cover glass, or injury to the instrument may result.

Write out this experiment in your notebook, describing exactly what you see. Explain just why the particles are moving. Why do the smallest particles move most? Do any of the particles take on a rotary motion? Is the motion here seen a proof of the existence of molecules, or merely evidence?

Exp. 2. Air Pressure and Rate of Evaporation.

Apparatus.—Two desiccators of about the same size and shape, one of them connected with a manometer and air pump, as seen in Fig. 1; a good air pump, preferably a mechanical pump run by a motor.
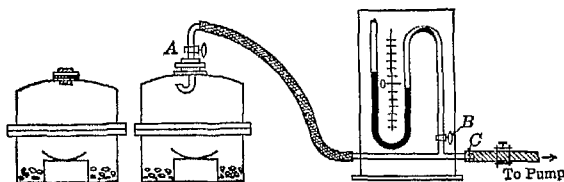
Fig. 1.

If a water pump must be used, the process of exhausting the air must not be stopped by turning off the water, or the latter will be drawn back into the manometer. Close cocks A and B (see sketch), and then pull off the rubber tube attached at C. The cock B may then be opened very cautiously, whereupon the mercury will be forced up into the end of the manometer tube. If the cock is opened too quickly the mercury will go over with a thud, probably breaking the tube.

Practically the same procedure must be followed where a motor pump is used. The cocks should be closed before the pump is turned off, and it is also well to have on the rubber tube near C a screw clamp, or stop-cock. This should also be closed before the pump is turned off, or oil may be thrown back into the manometer.

The easiest way to break the vacuum is cautiously to withdraw the stop-cock A, thus slowly admitting the air.

Procedure.—Place in a watch glass in each desiccator exactly 1 cc. of distilled water measured with a pipette. Close the desiccators, record the time, and then in the one case reduce the air pressure to about 2 cm. of mercury. When this is done, close the cock A and then turn off the pump as directed above. The two desiccators may now be left undisturbed.

After waiting about ten minutes it will be well to find whether the desiccator is "holding the vacuum." Proceed as follows: Leave the cock A closed, run the pump, if necessary, until the manometer again registers 2 cm., and then cautiously open A. The manometer should not show an increase in pressure.

Note the process of evaporation in the two cases, and when it is completed in one case remove the other watch glass and weigh to determine what weight of water has evaporated from it. From the different weights of water evaporated in equal time calculate the relative rates.

Explain fully what you have observed.

CHAPTER II

THE GAS LAWS

Exp. 3. Boyle's Law.

Apparatus.—The Boyle's law apparatus as seen in Fig. 2. Two glass tubes about 1 meter long and 6 mm. bore project upward from the mercury cistern A. One is closed at the top and contains the air whose volume and pressure are to be measured. The scale beside this tube indicates the volume. The other tube is open at the top and is intended as a manometer to indicate pressures. By means of a small bicycle pump attached through the stop-cock tube B air may be forced into the cistern so as to cause the mercury to rise in both the upright tubes. When the mercury stands at the same level in both tubes the pressure in the tubes is the same, and is equal to that of the atmosphere outside. When the mercury stands higher in the open tube the pressure in the closed tube is equal to that of the atmosphere plus the differences in the levels of the mercury. This difference in levels is read off by means of a sliding meter scale seen in the sketch (C).
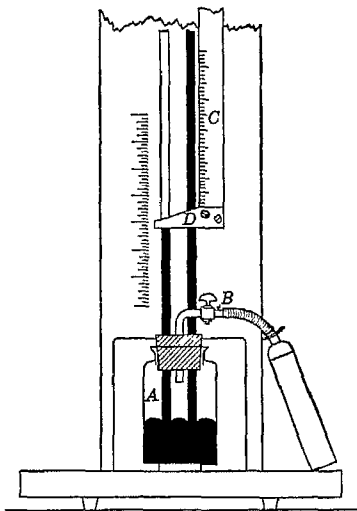
Fig. 2.

The tube leading from the pump contains a valve which prevents the recession of the mercury between strokes. This valve is not tight enough to depend on while making measurements: hence the stop-cock B. This stop-cock should be fastened in place by means of a rubber band to prevent leakage.

Procedure.—Pump up the apparatus so that the mercury in the manometer stands near the top of the tube. In doing this take short, quick strokes, and be very careful not to force the mercury out the top of the tube. When the pressure is sufficiently high catch the mercury

3

in position by quickly closing the stop-cock. After waiting a few moments to allow the vibration of the mercury column to cease and to be sure that there is no leakage, proceed to measure the volume and pressure. The volume, V, may be taken directly from the scale to the left, and should be read to hundredths of a cubic centimeter. To obtain the pressure, first read the barometer (in centimeters and tenths) and then adjust the sliding scale so that the metal gauge D at the end coincides exactly with the top of the mercury in the closed tube, and read off the difference in levels to 0.1 cm. The pressure P is the sum of the barometric pressure and the difference in levels. Calculate the value of PV.

Having determined one value for PV, cautiously open the cock B enough to allow the pressure to drop somewhat, say 10 cm., and then redetermine PV as directed above. This may be called $P'V'$, and should not vary from PV by more than two or three units out of a total of, say, 1750. This simply means that PV is a constant for any given quantity of gas, provided the temperature remains constant, as in this case.

Proceed in the same way to determine other values for PV until six or seven have been taken. Record the results thus:

V.	Differences in Levels.	Barometer.	P.	PV.

After having worked out the values for PV as above, obtain a sheet of centimeter coordinate paper and plot the values for P and V. Finally by use of a " French curve," draw a smooth line through the plotted points, obtaining thus the curve for Boyle's law. Since the values for P are much larger numerically than those for V it will be best to plot them to a larger scale.

Find the ratio between any two pressures and then find the inverse ratio between the corresponding volumes. Are they the same within the limits of experimental error? Are we right, then, in saying that the volume of a gas varies inversely as the pressure?

What name is applied to the curve obtained by plotting the Boyle's law data?

Exp. 4. Partial Volumes and Pressures of the Gases in the Air.

Apparatus.—The apparatus is such as is used in gas analysis for the absorption of the constituents of illuminating gas (Fig. 3). The tube A is called the " measuring tube." Tube B is the " leveling tube." The absorption pipette C contains metallic copper surrounded with a solution of ammonium chloride and ammonia. In the presence of oxygen copper goes into solution to form the blue complex, $Cu(NH_3)_4(OH)_2$. Oxygen is thus rapidly absorbed. The solution in the spherical bulbs serves to protect that in the pipette C.
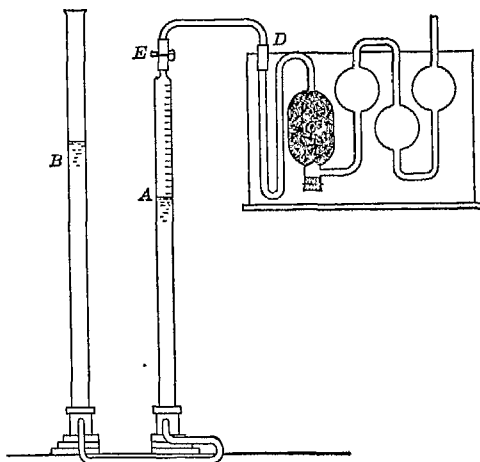
Procedure.—Disconnect the capillary tube at D, and then raise B until the water flows over• and expels *all*

FIG. 3.

the gas from the measuring tube A. Now lower B until the water in A stands at the 100-cc. mark, and that in B is at the same level. *While holding the tubes in this position* let another person close the pinch cock E. A now contains 100 cc. of moist air at atmospheric pressure.

First be sure that the absorption pipette C is entirely filled with liquid; then connect the capillary tube securely with D again, remove the pinch cock, and raise B until *all* the air goes over. With the tubes in this position, again put the pinch cock securely in place. Leave the apparatus now for ten minutes, shaking the absorption pipette occasionally to hasten the absorption of the oxygen. Finally run *all* the residual gas back into the measuring tube, and again close the pinch cock. After adjusting levels read the volume accurately..

After recording the volume, repeat the process of absorption to make sure that all the oxygen is removed. If the second reading of the volume agrees with the first the process may be considered finished. Record the final volume.

The gas left in the tube is mostly nitrogen, but contains some argon, and some water vapor, with traces of other gases. Let us first calculate the pressure which this mixture exerted when mixed with the oxygen. To this end find the atmospheric pressure by reading the barometer.

This was the total pressure including the sum of the partial pressures of all the gases. The nitrogen mixture left in the tube at the end of the experiment made up the same fraction of the total pressure as it did of the total volume, and what this was you already have the data to determine.

Having determined the pressure of the residual mixture, refer to the table in the manual, page 14, and obtain the pressure of the water vapor for the corresponding temperature. Determine then the pressure of the nitrogen mixture without the water vapor. Counting the pressure of the argon as 0.8 per cent of the total pressure and ignoring the trace of other gases, calculate the pressure of the nitrogen alone.

Now calculate the volume of the oxygen removed and then its pressure. This is done as in the case of the nitrogen mixture.

As a final summary of the experiment, write down the partial pressures of all the gases in the air as you have found them, and opposite each place its partial volume, that is, the number of cubic centimeters each would occupy at atmospheric pressure if removed as oxygen was.

	Pressure.	Volume.	
Nitrogen................			
Oxygen....			
Argon.........			
Water vapor....			
Other gases.............	trace	trace	
Totals			

(The partial pressures should total the barometric pressure and the partial volumes should total 100 cc.)

Exp. 5. The Coefficient of Expansion for Air.

Apparatus.—The most important part of the apparatus is a capillary tube closed at one end and containing a mercury index. The tube must have a uniform bore of about 1 mm. Select a tube with apparently uniform bore, and test by drawing in a column of mercury about 10 cm. long, and then measuring this column when in different positions. If the bore is uniform the column of mercury will have the same length wherever placed. Cut the tube 40 cm. long. To remove any possible traces of moisture from the inner surface of the tube force through it a gentle current of dry air while heating cautiously with a Bunsen flame.

When the tube is cool enough to handle, seal off *bluntly* 10 cm. from

one end. For introduction of the index draw out a piece of tubing until it is barely small enough to pass down into the capillary. If this tube is thrust into a deep layer of mercury and closed with the thumb, enough mercury may be withdrawn to form the index. This is then introduced by placing the end of the tube about 10 cm. down the capillary and removing the thumb.

Whenever the capillary needs drying out, the index may be thrown out and the tube heated while a current of air is drawn through it by means of a slender tube extending to the bottom. A new index is then introduced as above described.

Fig. 4.

It is a good thing to keep the tube connected with a calcium chloride drying tube when not in use. If no precaution is taken moisture will work in past the index, alternately condensing and vaporizing when the tube is used and thus introducing an error into the results.

The rest of the apparatus needs little description. B is a so-called Kjeldahl flask used in nitrogen determinations. It stands on the asbestos ring C during heating, to prevent superheating of the steam.

Procedure.—The length of the air column in the closed end of the tube is measured at two temperatures, and the expansion per degree is then calculated *in terms of the volume at* $0°$ C.

Arrange the apparatus first as seen in A, adjusting the bottom of the tube in the end of a cork so that the surface of the cork coincides with the end of the capillary, and holding the tube securely in place by means of a ring-stand. While the tube is in this vertical position accurately measure the length of the column of air below the index, tapping with a pencil to prevent any lag of the mercury, and taking care not to warm the tube or the thermometer with the hands. This length represents V_1. Also read the thermometer as accurately as possible (note 1). This reading is t_1.

Push the stopper a down the tube until its upper surface exactly coincides with the top of the index and then measure the distance down from the top of the tube.

Now connect the apparatus as seen in B, taking care that the thermometer and tube both clear the sides of the flask, and then heat the water to boiling, applying a small flame directly to the flask without
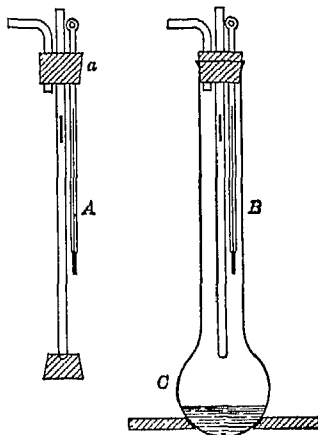
a gauze. The index will rise, of course, because of the expansion of the air below it. As it does this keep pushing the tube down through the stopper so that the upper edge of the index coincides with its upper surface, thus making sure that all the air column is heated. Finally, when the index no longer rises even after tapping with a pencil, again carefully measure the distance down from the top of the tube. The difference between this measurement and the former one will show the amount of expansion, and V_2 is, of course, equal to V_1 plus this expansion. Record the temperature as t_2.

When the data have been obtained, the calculation proceeds as follows: Let x equal the coefficient of expansion for air, that is, the fraction of its own volume at 0° C. which it .expands for each degree through which it is heated. Let 1 equal the volume at 0° C. At t_1 the volume will be $1+t_1x$, and at t_2 the volume will be $1+t_2x$. From this we obtain:

$$V_1 : V_2 :: 1+t_1x : 1+t_2x$$

Substituting your data in this equation, you can at once work out the value for x.

After thus obtaining the value as a decimal, transform it into a common fraction. The standard value for air is 0.003666 or 1/272.8.

NOTE.—For accurate work the thermometer should have been checked by comparison with an accurate standard thermometer.

Exp. 6. Graham's Law of Inverse Proportionality.

Apparatus.—A glass tube 1 meter long and of 2 cm. bore, with a tight-fitting cork for each end (Fig. 5). Two porcelain boats of equal size and small enough to pass easily into the ends of the
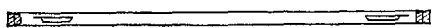
FIG. 5.

tube. The tube should be suspended in a horizontal position by means of two-ring stands.

Procedure.—Place in one of the boats a few cc. of concentrated hydrochloric acid and in the other a like amount of concentrated ammonium hydroxide (note 1). When the two boats are ready, place them in the two ends of the tube at the same time (this will require two people), and then immediately insert the corks. In about fifteen minutes the gaseous ammonia and hydrogen chloride will have diffused along the tube until they meet somewhere between the two boats. The point of contact will be marked by a sharply defined, disk-like cloud of ammonium chloride. Mark on the tube the point where this meeting occurs.

Now calculate where the meeting would occur if the distances

traveled by the two gases were inversely proportional to the square roots
of their densities,* and then compare with the observed values.

After making the above comparison, allow the process of diffusion
to continue for some time. A band of solid ammonium chloride will be
formed. Note the direction in which the band broadens and explain.

NOTE.—To make a fair comparison of the rates of diffusion the gases must
be of the same molecular concentration. This is approximately the case when the
solutions are of the concentrations recommended.

Exp. 7. Graham's Law and Molecular Weights.

Apparatus.—The glass cylinder A (Fig. 6) should be about 40 cm. high,
and 4 cm. in diameter. B is an unglazed battery cup, holding about 80 cc.

It is supported by a rubber stopper
and tube as seen. The rest of the
apparatus hardly needs description.
The amount of water in the bottle
C should be somewhat more than
sufficient to fill the cylinder up to
the stopper, but not enough to rise
into the porous cup. M and N are
paper markers.
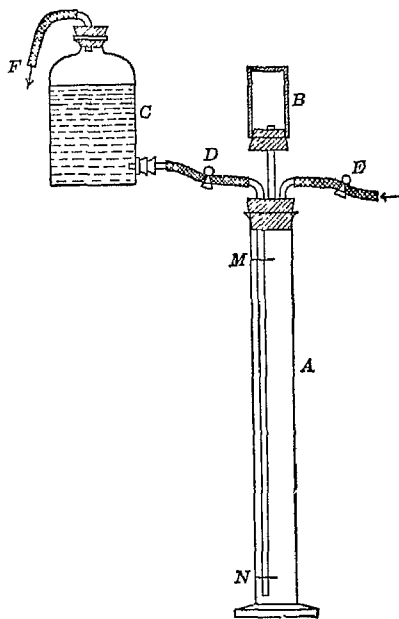
Procedure A. — Remove the
pinch-cock D entirely, so as to
allow free passage of the water,
and then, by means of a pump or
otherwise, apply a gentle suction
at F until all the water in the cyl-
inder has been displaced. Now
disconnect the pump, close E, and
allow the air to diffuse out through
the porous cup, noting, by means
of a stop-watch (or clock), the
exact time required for the surface
of the water in the cylinder to pass

FIG. 6.

from one marker to the other. Repeat the determination, obtaining
two concordant values. The average of these values may be recorded
as t (note 1). The average molecular weight of air is 29. This is to be
used as your standard of comparison in determining the molecular
weight of other gases.

* Prepare two simultaneous equations, thus:

$$x/y = \sqrt{17}/\sqrt{36.5}.$$
$$x + y = \text{length of tube.}$$

Procedure B.—Substitute carbon dioxide for air, running in the gas from a cylinder or generator, not too rapidly, and applying suction at F if necessary. After the cylinder is filled, the gas should be allowed to bubble through the water in the bottle C for several minutes. If this precaution is not taken, solution of the gas in the water will take place during the process of diffusion, and the time will thus be shortened. Having properly filled the cylinder, determine the time of diffusion as was done with air, obtaining two concordant values, and taking the average (t').

Calculating from your data, determine whether the times required for the diffusion of equal volumes of carbon dioxide and air are proportional to the square roots of the molecular weights, in other words, whether according to your data the proportion

$$t : t' :: \sqrt{m} : \sqrt{m'}$$

actually holds good.

Assume also that the molecular weight of carbon dioxide is unknown, and calculate its value from your data, using the equation

$$m' = \frac{t'^2 \times m}{t^2}$$

m in this case being 29, the molecular weight of air.

Procedure C.—Determine the molecular weight of the natural gas used in your burners. Do not forget the precaution concerning solubility.

Natural gas is usually nearly pure methane, CH_4, having a molecular weight of 16. Some samples, however, contain gasoline vapor. Gasoline is a mixture of hydrocarbons having an average molecular weight of about 100. Consequently, samples of gas containing this will have a higher molecular weight than pure methane. When the molecular weight is above 19 the gas is usually considered " rich " enough to work over for the gasoline it contains.

After determining the molecular weight of the gas, decide whether it would be profitable to work it over in this way.

Procedure D.—Determine the molecular weight of hydrogen, (note 2), proceeding as in the above cases. Hydrogen is not appreciably soluble in water, but the precaution about solubility must be observed, or the hydrogen will be mixed with a considerable amount of the gas last used.

In all these diffusion experiments it must be remembered that the gases are saturated with water vapor. In cases where the molecular weight of the gas is equal to, or near, that of water, this has no appre-

ciable effect on the rate of diffusion; but in the case of hydrogen, a gas of very low molecular weight, the effect is very marked. It is possible, however, to calculate a correction, and thus get a fair comparison of values. The average pressure of the mixture of hydrogen and water vapor during diffusion is about 76 cm. Of this pressure about 74 cm. are due to hydrogen (mol. wt. 2) and about 2 cm. to water vapor (mol. wt. 18). Calculate on this basis the average molecular weight of the mixture, and then compare with the experimental value.

NOTES.—(1) The time for air should be about ten minutes. ˙
(2) If a pressure cylinder is used a pressure regulator must be attached.

CHAPTER III

LAWS GOVERNING CHANGE OF STATE

Exp. 3. Vapor Pressure of Water.

A known volume of air saturated with water vapor is drawn through a calcium chloride tube where the water is absorbed and weighed. From the weight of this water the vapor pressure is calculated.

Apparatus.—The sketch (Fig. 7) shows the general arrangement. The 12-inch tower A contains wool which has been wet and then squeezed
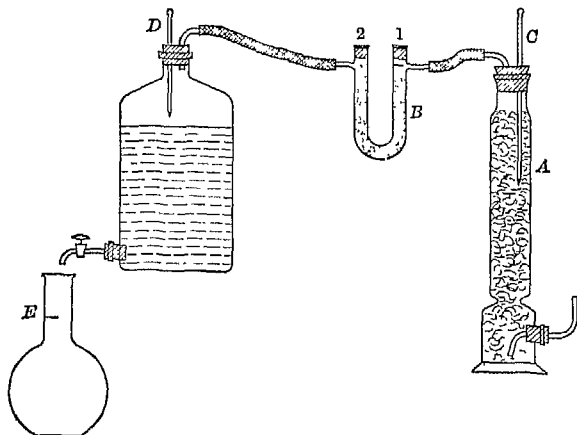
FIG. 7.

as dry as possible. It should be packed rather loosely, but in such a way as not to leave any channels through which the air may pass without coming into very close contact with it.

The 5-inch U-tube B contains granulated calcium chloride of wheat-grain size, well shaken down. At the top of each limb is a loose plug of asbestos intended to prevent the expulsion of any fine dust from the surface.

All so-called "anhydrous" calcium chloride contains some water of hydration, and its effectiveness as a drying agent depends on the amount of this water present. It also usually contains some calcium oxide, which absorbs carbon dioxide from the air and thus changes weight. To correct both of these defects, the tube, after being filled, is

suspended up to the side arms through a slot in the cover of an air bath, and heated to 275° C. while a slow current of dry carbon dioxide is conducted through it. This process should continue for at least an hour. A good way to tell when the water is all removed is to place a cold glass tube over the exit arm of the U-tube and note whether there is any condensation of moisture. When calcium chloride is thus treated it becomes almost anhydrous, and the surface is left in a fine, porous condition. According to A. T. McPherson * the reagent thus prepared takes on much water by simple adsorption on the surface of the particles before the formation of a hydrate begins, and its drying capacity during this process is almost as perfect at that of P_2O_5, the best drying agent known. Its efficiency in this capacity also depends, of course, upon the length of the column and upon the slowness with which the air is drawn through.

At the end of the drying process the U-tube is disconnected from the CO_2 generator, and while it is still hot, dry air is drawn through it to displace the CO_2. (Why is this necessary?) Subsequent drying may be done with air alone.

In the use of this drying tube the following precautions should be observed:

(1) Keep the arms of the tube closed when not in use to prevent access of moisture. (Rubber connectors containing large glass beads are good for this purpose.)

(2) Keep the surface of the tube perfectly clean and bright; otherwise the weight cannot be absolutely depended on.

(3) Always run the current of air in the same direction. If the tube is used in one direction and then reversed, much of the water already absorbed will be expelled. It will be well to mark the stoppers " 1 " and " 2 " to guard against this.

The thermometer C must be accurate to 0.1°, or at least the data for a correction must be at hand. An error of 0.1° in reading the thermometer will (at 20°) produce an apparent error of about 0.1 mm. in the vapor pressure. (Prove this.)

D is a common thermometer which, however, should be correct to at least 1° C.

The flask E is graduated to hold some definite amount, say 4.5 liters; the amount should not be much less than this.

It is scarcely necessary to say that the connections must be secure. Those attached to the U-tube must, however, be easily removable without breaking the tube. · In removing a connector from the arm of a U-tube, be sure to grasp the tube on the side near the arm; if the connector

* Jour. Am. Chem. Soc., July, 1917.

sticks, roll it back with the thumb, twisting gently at the same time. Do not pull it and thus cause it to grip the tube all the tighter.

Procedure.—Disconnect the U-tube from the rest of the apparatus, place it flat upon the balance pan, and weigh accurately to the fourth decimal place. To be sure that the air pressure inside the tube is the same as that of the atmosphere, the side arms may be left open while weighing. Connect the weighed U-tube in its place so as to allow the air to pass in the proper direction, and then start the water from the aspirator bottle into the graduated flask. It may run rapidly enough to form a barely continuous stream. Record the temperature as read on both the thermometers, remembering to read the one where the saturation occurs to 0.1°, and correcting the reading if necessary.

When the proper volume of air has passed through the apparatus, turn off the aspirator and then disconnect the U-tube for weighing. At the same time also read the temperature on the two thermometers and record with the first readings. Finally weigh the U-tube as before and calculate the weight of the water collected.

You now have the data for calculating the members of the equation $PV = nRT$, and when this is done the value for P can at once be determined. Thus, if the average of the two readings on thermometer C is within 1° of the average for D the volume of water run off represents the volume, V, of saturated water vapor run into the U-tube; if not, the correct volume must be calculated by the use of Charles' law. T is the average of the two readings on thermometer C, reduced, of course, to the absolute scale; n is, of course, the fraction of a mole of water collected.

Calculate P by use of the equation given above, remembering that the value thus obtained will be some fraction of an atmosphere, and finally translate the value into millimeters. Compare this value with that obtained by interpolation from the table below. Your value should not differ from this by more than 0.2 mm.

VAPOR PRESSURE OF WATER IN MILLIMETERS

Temperature.	Pressure.	Temperature.	Pressure.
15	12.7	21	18 5
16	13.5	22	19 7
17	14.4	23	20.9
18	15.4	24	22.2
19	16.3	25	23.6
20	17.4	26	25.1

Exp. 9. Heat of Vaporization of Water.

Apparatus.—As seen in Fig. 8. The Erlenmeyer flask A is of 500-cc. capacity. The trap B is 2.5 by 12 cm. The tube E serves to draw off the water which accumulates from condensation. The 400-cc. calorimeter beaker C stands in a 1-qt. graniteware cup, and is insulated by packing about loosely with cotton. It is covered by means of a piece of cardboard cut as seen at F. The transite board D serves to, protect the calorimeter from the heat of the flame.
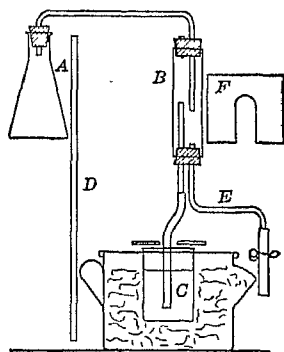
The apparatus should be carefully constructed according to the sketch, and offered for inspection before it is used.

Procedure. — Weigh the calorimeter beaker accurately on the laboratory balance, fill about two-thirds full of distilled water which has previously been cooled to about 5° C. by addition of ice water

FIG. 8

(note 1), and then weigh again. In the meantime heat the water in the Erlenmeyer flask to rapid boiling. Now pack the calorimeter in the cup as seen in the sketch, and immediately take the temperature to 0.1°, stirring well while doing this. Call this t_1. When this is done immediately thrust the steam tube into the water, cover the calorimeter, and then allow the condensation to proceed until the temperature of the water is as much above room temperature as the original temperature was below (note 2), *stirring well* each time before reading. Now quickly push the calorimeter to one side so as to withdraw the steam tube, *stir well*, and immediately take the temperature, t_2, keeping the calorimeter covered as much as possible. Finally remove the calorimeter, and weigh as at first. The increase in weight gives the amount of steam which has condensed.

The calculation is made as follows: The original weight of water multiplied by the change in temperature ($t_2 - t_1$) gives the heat absorbed by the water. But the glass has also been heated. One gm. of glass requires 0.2 calorie to raise its temperature 1° C. We may therefore calculate the heat absorbed by the glass by multiplying its weight by 0.2 and then by the change in temperature. Or, if we choose, we may calculate the water equivalent of the glass, which is 0.2 its weight, and· this may be added to the weight of the water before the heat absorbed by the latter is calculated. At any rate the total amount of heat absorbed is the sum of the amounts absorbed separately by the water and the glass.

Now the total heat absorbed has come from two sources: (1) from the condensation of the steam at 100° and (2) from the cooling of the water thus condensed from 100° (note 3) to the final temperature, t_2. The latter must be calculated by multiplying the weight of the water condensed by its change in temperature $(100° - t_2)$. If we subtract the heat so liberated from the total heat absorbed we shall have the heat liberated by the steam in condensing at 100°.

To get the heat liberated by the condensation of 1 gm. of steam at 100° (the heat of vaporization) we must divide the amount last calculated by the total weight of water condensed.

NOTES.—(1) Be careful to see that no pieces of ice are present when weighing. (Why?)

(2) By beginning below room temperature and ending above we shall have a balancing of errors; the water at first takes up heat from the air and later gives it off.

(3) The boiling-point of water is not quite 100° C. at our average pressure. See " Boiling-point of Water," Handbook of Chem. and Phys.* The value here found should be used in the calculation.

* Published by the Chemical Rubber Co., Cleveland, O.

CHAPTER IV

MOLECULAR WEIGHTS

Exp. 10. Molecular Weight of Carbon Dioxide.
Apparatus.—A 250-cc. Erlenmeyer flask fitted with tubes and pinch cocks as seen in Fig. 9. The external ends of the tubes, and the connectors E and F must be short, or difficulty will be experienced in getting the flask upon the balance pan. Also the tube connected with E must not extend below the stopper. There should be a mark on the

From CO_2 generator

C   F   E

B   Cotton

A

CaCl$_2$

NaHCO$_3$
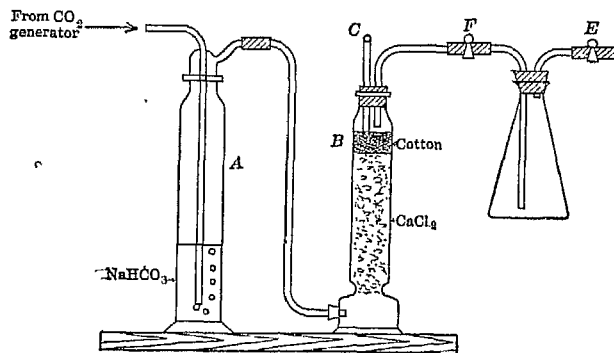
FIG. 9.

neck of the flask to which the stopper is always adjusted in order that the capacity may not vary. It is hardly necessary to say that the flask should be clean and dry and free from finger marks (note 1).

The other pieces of apparatus shown in the sketch are a gas wash bottle A and a calcium chloride drying column B. A carbon dioxide generator or a pressure cylinder is needed, but is not here shown.

The thermometer C measures the temperature of the gas.

Procedure.—Take the clean, dry flask prepared as above, open one of the pinch cocks so that the pressure inside the flask shall be the same as that of the atmosphere, and then weigh carefully to the third decimal place.

Now, from a generator or pressure cylinder, fill the flask with air-free carbon dioxide (note 2). The gas should pass, first through a solu-

17

tion of sodium bicarbonate contained in the wash bottle A (note 3), and then through the drying column B. The current should not be too rapid, or the washing and drying may not be complete. The bubbles may pass about as rapidly as a watch ticks. Let the gas enter the flask through the longer tube, as seen in the sketch. (Why?) After the process has continued for about ten minutes, close the pinch cocks, and remove the flask to the balance for weighing.

After weighing, again connect the flask with the generator as before, and pass the carbon dioxide through it for another five minutes. In the meantime take the temperature and barometric pressure: Finally, weigh the flask again. If the air was all removed on the first trial there will be no change in weight. (Why?) A very slight change is allowable, say 1 mg.

The weight of the carbon dioxide is the difference between the weight of the flask full of the gas and the vacuous flask, and its volume is, of course, the volume of the flask. Both the weight of the vacuous flask and its capacity are, therefore, to be determined.

Determine the capacity of the flask by filling with water up to the pinch cocks and weighing on the *laboratory* balance. The weight of the water, and so its volume (note 4), may be taken as the difference between the weight of the flask in air and the above weight. To find the weight of the vacuous flask we must know the weight of air it contains at the observed temperature and pressure. This may best be determined from the table, "Density of Dry Air," Handbook of Chem. and Phys., where the weight of 1 cc. of air for any ordinary temperature and pressure is given. Knowing the weight of the flask filled with air and the weight of the air contained in it, determine the weight of the vacuous flask.

You now have all the necessary data, namely, the weight of the flask filled with carbon dioxide gas, the weight of the vacuous flask, and the temperature and pressure of the gas when collected. If you determine the weight of the gas and then reduce its volume to standard conditions you will have the weight of a known volume under standard conditions. You then have only to find the weight of 22.4 liters under the same conditions. This will be the molecular weight. For the sake of the practice, make the calculation also by use of the equation $PV = wRT/M$.

NOTES.—(1) "Bon-ami" or some similar preparation is good for cleaning glass. When an article is properly cleaned, water adhering to the surface will not creep up into drops but will form a continuous film. A solution of chromic acid in sulphuric acid (best made by mixing about 10 gm. of powdered $Na_2Cr_2O_7$ with 300 cc. of crude, concentrated sulphuric acid) is very good for removing traces of grease from the inside of apparatus or any place which cannot be reached with other cleaners. This should, however, be used with great care, due to its very corrosive nature. Never

leave any on the outside of the bottle to get upon the hands or clothing or to spoil the desk top.

Articles cleaned in any way must be carefully rinsed first with tap water and then with distilled water.

To dry out apparatus after cleaning, first throw out as much water as possible by swinging the piece violently down at the side, then heat gently over a gauze (not over a direct flame), rotating constantly, and at the same time conduct into the piece a *gentle* stream of air from the air-blast line.

(2) The carbon dioxide from a pressure cylinder is not likely to contain much air, but that from a generator may contain a considerable amount, depending on the length of time the generator has run since refilling.

(3) The carbon dioxide is likely to contain a little hydrochloric acid gas from the generator. (Why?) By interaction with sodium bicarbonate the latter is absorbed, an equivalent amount of carbon dioxide being set free. Why would normal sodium carbonate, Na_2CO_3, not do just as well?

(4) One gm. of water occupies a volume of 1 cc. only at 4° C., and this means 1 gm. weighed in a vacuum. Weighed in air, the water is buoyed up somewhat, and so more is required to give an apparent weight of 1 gm. At 20° C. the volume of water corresponding to an apparent weight of 1 gm is 1.003 cc. The difference may, however, be neglected in this case.

Exp. 11. Molecular Weight of Ether.

Apparatus.—A Dumas bulb in which the end of the sealing tube has been replaced by a rubber connector bearing a pinch cock. The connector is securely fastened in place by wiring, and the end of the wire is turned into a loop by which the bulb is suspended when being weighed. The bulb may be dried out as usual (note 1, Exp. 10), the only requisite being the use of a very slender metal tube to conduct the air in. There will also be needed a 3-qt. graniteware bath, a bulb holder, and a funnel with a long, slender stem to be used in getting the ether into the bulb. The latter may be made by drawing out the stem of a thistle tube.
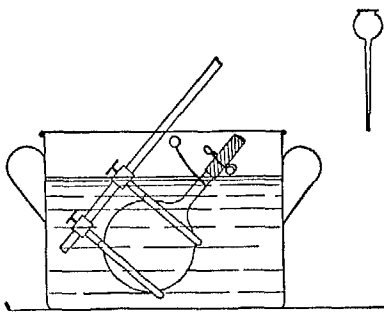
FIG. 10.

Procedure.—Determine the weight of the bulb filled with air at the temperature and pressure of the balance room; that is, leave the bulb hanging in the balance case with the pinch cock open for a few minutes before weighing. In the meantime have water heating in the bath for the submersion of the bulb. It should be heated to about 90° C.

Put about 10 cc. of pure, dry ether in the bulb, *turn out all flames in the vicinity*, and then by means of the holder place the bulb under the hot water as seen in the sketch, taking pains not to allow the outlet tube

to become submerged.   Stir the bath constantly by means of a mechan-
ical stirrer or by slowly moving the bulb back and forth in a lateral direc-
tion.   Watch for the ether to boil away completely, and after this has
occurred wait about two minutes for the vapor to gain the temperature
of the bath (note 1) taking care not to raise the bulb in the meantime
(note 2).   Finally take the temperature of the bath as accurately as
possible, close the pinch cock securely, and then remove the bulb and
wipe it dry.   Hang the bulb now in the balance case, and after allowing
ample time for temperature adjustment, weigh.   In the meantime read
the barometer.

To obtain the capacity of the bulb, fill with water and weigh.   The
filling is easily accomplished if, with the bulb still closed, the outlet tube
is placed under water and the pinch cock then removed (note 3).   If the
bulb does not fill completely by this method, it is due to the presence
of air which was not expelled when the ether boiled away or which may
have leaked in during the weighing.   A small bubble is permissible.
The filling must be complete before the bulb is weighed, of course.

Having thus determined the capacity, determine the weight of the
vacuous bulb as directed under Exp. 10.   Calculate then the weight of
the ether vapor.   You then have the weight of a known volume of gas-
eous ether at a known temperature (the temperature of the bath) and
at a known pressure (the pressure of the air).   Reduce the volume to
standard conditions, and then calculate the molecular weight in the
usual way.

NOTES.—(1) While the ether is boiling away the vapor is at its boiling-point,
34° C.

(2) If the flask is raised after the liquid is all boiled away, the vapor will con-
tract and air will enter.

(3) When the bulb was cooled for weighing, much of the ether vapor condensed
to a liquid, as you doubtless noticed.   This, of course, much reduced the pressure,
and thus made possible the entrance of the water.   The ether vapor still in the bulb
dissolves in the water, still further lowering the pressure and thus insuring almost
complete filling if no air is present.

CHAPTER V

THE LAWS OF COMBINATION

Exp. 12.—The Composition of Silver Oxide.

Apparatus.—An air bath made from a quart graniteware cup, shaped as seen in the Fig. 11; also stirring rods, and a desiccator as shown in Fig. 12.

To distribute the heat more evenly, the air bath contains a star-shaped diaphragm of iron or tin. The points of this are bent down to
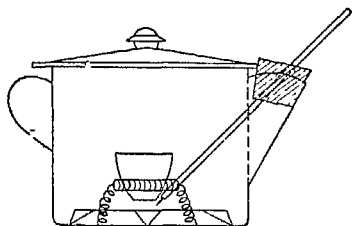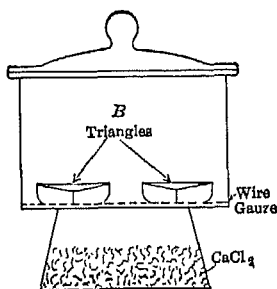
FIG. 11   FIG. 12.

serve as legs, thus bringing the diaphragm about half an inch above the bottom of the bath. The triangle bearing the object to be heated stands astride the diaphragm, but high enough to prevent contact of the object with it. The thermometer is inserted through a cork cut to fit the spout of the cup, and projects over the diaphragm as near the triangle as possible. By means of an ordinary Bunsen flame temperatures up to 300° C. may be maintained. In using the bath a constant temperature should be secured *before* the object to be heated is put in. For low temperatures it will be best to use a small luminous flame, which is more likely to be steady.

The following table, showing the approximate relationship between size of flame and temperature, will be helpful: *

* Natural gas at a pressure of about 6 oz. was used.

21

Size and Nature of Flame.	Temperature.
1-inch, luminous, 2 inches from bath	100° C.
2-inch, luminous, 1 inch from bath	135° C.
2-inch, non-luminous, 1 inch from bath	145° C.
3-inch, non-luminous, just touching bath.	180° C.
4-inch, non-luminous, air well regulated.	240° C.
5-inch, non-luminous, air well regulated.	300° C.

Temperatures higher than 300° C. should not be used, or the enamel on the bath will be melted.

The stirring rods should be about 17 cm. long and not more than 4 mm. in diameter. The ends must be nicely rounded by heating in a Bunsen flame. The rods must in *no case* be used without this. It is well to have one rod tipped with a short piece of *small* rubber tubing, which should be allowed to project slightly over the end. This is sometimes indispensable for removing the last traces of a precipitate from a beaker.

The desiccator should be carefully cleaned, both inside and outside. If it already contains dry calcium chloride this may be left in. If not, have the store-room keeper fill the bottom part about half full, pouring in the calcium chloride through a funnel so as not to dust the upper part of the desiccator. A diaphragm of wire gauze rests on the shoulder above the calcium chloride, and upon this should stand one or more triangles having the ends bent down to form legs about three-fourths of an inch high. A crucible placed in a desiccator to cool always rests on the triangle, not on the diaphragm. Other objects, for example a weighing bottle, may rest directly on the diaphragm. The cover of the desiccator is made air-tight by means of a very thin coat of vaseline. An excess should be avoided.

All the above pieces of apparatus should be in order before any experimental work is even begun. Ask to have them inspected.

Procedure.—First prepare silver oxide as follows: Weigh out on the laboratory balance about 4 gm. of silver nitrate, and dissolve this in about 50 cc. of distilled water. Now take a stick of sodium hydroxide 1 in. long, " pure by alcohol " (note 1), wash the carbonate from the surface (note 2), and dissolve in 25 or 30 cc. of distilled water. Next mix the two solutions in a 300-cc. casserole, and stir well, testing also to see if there is an excess of the alkali, and adding more if necessary. (Why have an excess?) After the silver oxide has settled down almost completely, carefully pour off the liquid without wasting any more of the precipitate than can be avoided. Wash the silver oxide four times by decantation; that is, add about 200 cc. of distilled water, stir thoroughly and allow to settle, and then pour off the liquid as at first, repeating the process four times. This process should remove all the sodium

nitrate and the excess of alkali. Drain off the water, and then dry the product on a steam bath. To remove the last traces of water, powder the oxide in a small evaporating dish, and then heat in the air bath for one hour at a temperature of 148° C. Great care should be taken to maintain the temperature and not allow it to rise higher (note 3). If at any time it is seen to be going too high, it may be checked instantly by removing the cover of the air bath.

As soon as the heating is completed, transfer the silver oxide to a weighing bottle, and as a double precaution against moisture keep this in a desiccator.

When the silver oxide is ready, clean and ignite a No. 0 porcelain crucible. Allow this to cool somewhat on the triangle (note 4), remove it to a desiccator, and when perfectly cold (note 5), weigh accurately to the fourth decimal place. After recording the weight of the crucible, place another 1-gm. weight on the balance pan, and then place in the crucible enough of the silver oxide to again restore equilibrium. Great care must be taken not to get a particle of the oxide on the balance pan, or the weight of the sample will be in error by just this amount. In getting the final adjustment of the equilibrium very exactly, a steel spatula must be used, as this makes it possible to transfer very small amounts of the oxide.

Now remove the crucible to a triangle resting on a *ring stand*, cover, and heat, at first gently, with the flame some distance below the crucible. Finally, when most of the oxide is decomposed, heat to faint redness for a moment. Allow to cool as mentioned above, and when perfectly cold, weigh.

From the data obtained in this experiment calculate the percentage of silver in silver oxide. The exact value is 93.09 per cent.

Save the pure silver formed in this experiment for use in the next experiment.

NOTES —(1) " Pure by alcohol " means that the sodium hydroxide has been dissolved in alcohol, and thus separated from such impurities as sodium chloride which do not thus dissolve. If chloride were present, the silver oxide would be mixed with silver chloride. (How would you test for chloride in the NaOH?)

(2) Because of the action of the carbon dioxide in the air, sodium hydroxide always contains some carbonate, especially on the surface of the sticks. This may be dissolved off and thrown away.

(3) Silver oxide is decomposed completely into silver and oxygen at 250° C. It probably begins to decompose at 200° C. At 145°–150°, however, there seems to be little or no decomposition, and this temperature is necessary to get rid of all the water.

(4) If a red-hot crucible is put immediately into a desiccator the latter is heated so much that a long time is required for the temperature to become normal again. It is best to allow the crucible to cool so that it can barely be touched without discomfort.

(5) If an object is weighed while still warm, an upward current of air will be developed around the balance pan, and the object will appear to weigh less than it really does.

Exp. 13. Composition of Silver Chloride.

Apparatus.—A Gooch perforated crucible, a suction flask to go with it, a water suction pump, and a wash bottle.

The Gooch is a slender porcelain crucible with a perforated sieve-like bottom upon which a mat of asbestos is formed. This, when held in place by a porcelain disk or a layer of glass beads, forms the filtering medium. When properly constructed, this mat filters as well as the best paper, and has two additional advantages: it does not break when suction is employed, and it can be directly weighed. If a paper is used it must be gotten rid of by burning before the substance upon it can be weighed, and in many cases the burning of the paper causes serious change in this substance.

For the preparation of the Gooch filter, consult the instructor. The general procedure is, however, as follows: Fasten the crucible in place by means of the rubber stopper or a piece of rubber tubing as shown in Fig. 13, apply suction, and float in enough asbestos to make a mat about 1/32 inch thick (note 1). Place upon this mat the disk or beads, and then wash with distilled water. Break the suction by pulling off
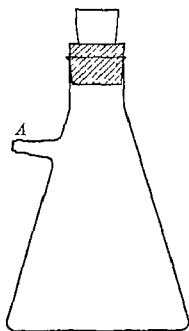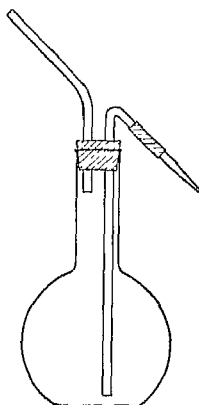
Fig 13.   Fig. 14.

the rubber tube attached at A (not by turning off the pump), remove the crucible, wipe with a clean towel, and then dry completely by setting in a common crucible and heating gently on a triangle. The outside crucible may finally be heated nearly to redness. Cool in a desiccator for the usual time, and then weigh.

The wash bottle is fitted up according to Fig. 14. The stopper is

of rubber, not cork.   In bending the tubes use a flat flame, not a Bunsen flame.   The bends must be perfectly smooth and round, and all ends must be fire-polished.   The neck of the flask is wrapped with candle wicking so that it may be handled while containing hot water.

After fitting up the apparatus as directed, have it inspected before use.

Procedure.—First prepare and weigh the Gooch crucible as directed above, then return it to the desiccator and allow it to remain there until needed.

Take the pure silver formed in Exp. 13 and already weighed, carefully loosen from the crucible by means of a steel spatula, and transfer to a 300-cc. beaker.   Be very sure that this removal is complete and that no particles are lost.   Pour over the silver in the beaker 10 cc. of 1 : 1 nitric acid, and immediately cover.   Also rinse the crucible with a little of this acid, and add this to the main portion.   Warm the beaker, if necessary, to hasten solution.   When every trace of the silver is dissolved, wash down the cover glass and the sides of the beaker with distilled water, and then dilute the solution to about 150 cc.   (Do not measure.)

Now heat the solution nearly to boiling, and then add slowly, with constant stirring, 5 cc. of 6 N hydrochloric acid.   Continue the stirring and heating until the precipitate has thoroughly coagulated and the liquid above it is almost clear.   It is then possible to tell by adding a little more acid whether precipitation is complete.   If, when the acid is added, a turbidity is produced, more acid must be added until the precipitation is complete.

When precipitation is complete put the weighed Gooch crucible in place on the suction flask, start the pump, and then filter the solution as rapidly as it can be drawn through.   Finally wash the chloride into the crucible, cleaning out the last traces adhering to the glass by means of a rubber-tipped rod (a " policeman ").   Since no solids are present in the solution, it is not necessary to wash the chloride any more than will be done by getting it all into the crucible.

When the pump has removed as much of the water as possible from the chloride, remove the crucible, and dry as noted above, only do not heat so strongly (note 2).   The safest way is to put the crucible in the air bath and heat to about 200° C. for half an hour.   After being thus heated and cooled, the crucible and contents are weighed, and then the heating is repeated; if on second heating there is no further loss in weight, the process is stopped.   This is called " heating to constant weight."

Having determined the weight of the silver chloride, calculate from

this and the weight of silver taken the percentage composition of silver chloride.   The accepted values are: silver 75.26 per cent, chlorine 24.74 per cent.   Your values should not differ from these by more than 0.2 per cent.

Place the silver chloride in the bottle marked " silver residues."

NOTES.—(1) The asbestos used in a Gooch filter is prepared especially for the purpose by boiling up with dilute hydrochloric acid, and then washing to remove any soluble matter.   It is then stirred up with a large amount of water, and both the finest and the coarsest fibers are rejected.

(2) Silver chloride melts at 460° C.; if heated to a much higher temperature, it volatilizes.   It is usually considered allowable to heat until it just begins to melt around the edges.

Exp. 14. The Multiple Proportions of Chlorine in the Chlorides of of Mercury.

Procedure A.—First prepare and weigh a Gooch crucible.   Next, clean, dry and weigh a 7-cm. porcelain evaporating dish.   When the correct weight has been added to balance the dish, add another 1-gm. weight, and then by means of a steel spatula carefully place in the dish enough mercurous chloride to restore equilibrium.   Record only the weight of the sample thus weighed.

Now treat the chloride with a solution containing 0.5 gm. of sodium hydroxide (free from chloride) in 25 cc. of water, and heat on the steam bath for fifteen minutes (note 1) with frequent stirring.   (Do not withdraw any of the solution when removing the rod.)   At the end of this time dilute the solution somewhat and then filter and wash the precipitate until free from chloride.

To the alkaline filtrate containing the chloride now add dilute nitric acid until, after thorough stirring, a minute piece of litmus paper previously placed in the liquid shows a distinct acid reaction.   (Why is this done?)

Dilute the solution (if necessary) to about 150 cc., heat nearly to boiling and then precipitate the chloride radical as follows: Add, with stirring, 25 cc. of N/5 silver nitrate solution, and then continue the heating and stirring until the solution clears.   Test then for complete precipitation by use of a few more drops of the silver nitrate.   Be sure that the precipitation is complete, but do not add an excess of the reagent.

Proceed now with the filtration, as directed under the last experiment, but remember that in this case the solution contains salts (what salts?) which must be washed out.   Five or six washings with hot water will not be too much.   The drying and weighing are also conducted as under the last experiment.

After the weight of the silver chloride is obtained find the weight

of chlorine originally contained in 1 gm. of mercurous chloride; and finally calculate by proportion the weight of chlorine which would be combined with 1 *gm. of mercury* in this compound.

Procedure B.—Weigh out a 1-gm. sample of mercuric chloride, proceeding as above. Dissolve in 20 cc. of hot water, add a solution containing 1 gm. of sodium hydroxide, stir, and heat on a steam bath until the precipitate has thoroughly settled (note 2). From this point proceed as directed in Procedure A, with the following exception: Use 40 cc. of N/5 silver nitrate solution in precipitating the chloride radical, instead of 25 cc. The Gooch crucible may be used with the former precipitate in it.

After the weight of the silver chloride is found, calculate as above the weight of chlorine combined with 1 *gm of mercury* in mercuric chloride.

Having analyzed the two chlorides of mercury, note the relationship between the two weights of chlorine, each combined with one and the same weight (1 gm.) of mercury. Calculate also the equivalent weight of mercury in the two cases.

Please put the silver chloride in the silver residues bottle.

NOTES.—(1) Although the mercurous chloride is nearly insoluble in water, it reacts with sodium hydroxide according to the equation

$$2NaOH + 2HgCl \rightarrow 2NaCl + Hg_2O + H_2O$$
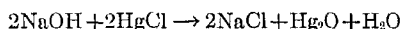
and if time enough is allowed, the reaction is nearly complete. Heat hastens the process. The chloride radical, which is to be determined, is thus transferred from the mercury to the sodium, and is, of course, found in the filtrate with the excess of alkali It is necessary to get it into this form before it can be precipitated with silver nitrate, as this reagent does not react with mercurous chloride.

(2) If the mercuric chloride were finely powdered the reaction would slowly proceed to completion upon simply treating the solid directly with the alkali; but it is always best to carry out such an operation in solution where the reaction is practically instantaneous. This reaction is represented by the equation

$$HgCl_2 + 2NaOH \rightarrow HgO + 2NaCl + H_2O$$
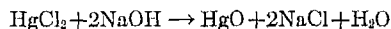
The treatment with NaOH is necessary, even in the case of this soluble chloride, since silver nitrate does not completely precipitate the chlorine in presence of mercury.

Exp. 15. The Law of Volumes from the Analysis of Ammonia.

Ammonia gas, generated by heating strong ammonium hydroxide and dried by passing over soda-lime, is led over hot copper oxide, where the hydrogen is removed to form water. The nitrogen passes on and is measured. Data are also obtained as to the volume of hydrogen originally combined with the nitrogen and of the ammonia decomposed.

Apparatus.—A 250-cc. Erlenmeyer flask, a 6-inch U-tube, and an 8-inch combustion tube of thin, hard glass with tapering ends, as shown in Fig. 15.   Any bottle will do for collecting the gas, e.g., one of the 600-cc. glass-stoppered bottles of the regular outfit.   All connections
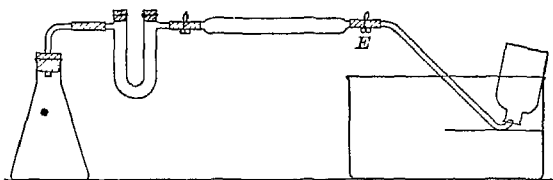
Fig 15.

must be perfectly secure.   Use rubber stoppers, and *test* the apparatus for leaks before use.

Procedure.—Fill the combustion tube with copper oxide (the wire form) and fasten in place by means of a wad of long fiber asbestos placed near each end.   To make sure that this oxide contains no water, connect the tube to a pump and draw through it a slow current of *dry* air while heating moderately with a burner.   Allow the tube to cool, and weigh when perfectly cold.

While the tube is cooling fill the U-tube with granulated soda-lime, and close with rubber stoppers (note 1).   Also place in the flask about 100 cc. of the strongest ammonium hydroxide solution.

Finally, when the combustion tube has been weighed, connect the parts of the apparatus as seen in the sketch.   Do *not* put the delivery tube under the bottle, and do not forget the pinch cocks.

Now warm the flask gently (note 2) and watch the bubbles as they issue from the delivery tube.   Air is insoluble (nearly) in water, but ammonia is very soluble.   Therefore, when all the air is expelled from the apparatus the bubbles will cease to rise through the water.   When this occurs place the delivery tube under the bottle and then immediately begin heating the combustion tube.   The heating should be gentle at first, the flame being waved back and forth, and great care should be taken not to burn the rubber connectors.   Later, heat strongly until the oxide decomposes the ammonia, and nitrogen is evolved (note 3) Do not allow the water to condense at the end of the tube.   When the bottle is about one-third full, or when the copper oxide is nearly all reduced, stop heating the tube, but allow the ammonia to pass until all the nitrogen is swept over.   Finally stop warming the ammonia flask, carefully watch the delivery tube until the water begins to recede (Why does it recede?) and then quickly put the clip *E* in place.   Allow

the tube to cool without disconnecting (note 4). When cold, disconnect, draw out the ammonia with a pump (Why?), and then weigh.

Since a good deal of ammonia has been run into the pneumatic trough, the nitrogen collected will contain some ammonia, and this must be removed before the nitrogen can be measured. To accomplish this, stopper the bottle securely, and transfer to another trough containing clean water, setting over one of the holes in the shelf. To hasten the removal of the ammonia, attach a rubber tube to the water faucet and run a stream of water up into the bottle from below, first driving the air from the tube, of course.

Finally measure the nitrogen in the usual way, and calculate the volume down to standard conditions, not forgetting to allow for water vapor. Calculate also the weight of the nitrogen from its volume.

The loss in weight suffered by the copper oxide represents the oxygen removed from it. This oxygen has united with the hydrogen of the ammonia to form water. Knowing the composition of water, you can immediately calculate the weight of this hydrogen, and from its weight you can then calculate its volume under standard conditions. Remember that this is the hydrogen which was originally combined with the nitrogen you have collected.

Adding together the weights of the nitrogen and the hydrogen will give the weight of the ammonia decomposed. From this weight the volume may be calculated as in the other cases.

Having thus found the volumes of the nitrogen and hydrogen and of the ammonia from which they came, you will at once notice the extremely simple and exact relationship. State this relationship.

NOTES.—(1) Soda lime is used to dry the ammonia, since calcium chloride or sulphuric acid would combine with it. "Quicklime" (calcium oxide) might be used, but is not so good.

(2) Use a flame about half an inch high. Great care must be taken that the warming is not interrupted by draughts of air or otherwise. If this happens, water will be sucked back into the combustion tube

(3) Copper oxide reacts with ammonia thus:

$$3CuO + 2NH_3 \longrightarrow 3Cu + 3H_2O + N_2$$
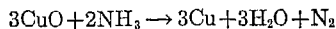
(4) If the tube is opened while still hot, air will enter and oxidize the copper, thus changing its weight.

CHAPTER VI

ATOMIC WEIGHTS

Exp. 16. Specific Heat and Atomic Weight of Tin.

The specific heat of tin is determined by the so-called "method of mixtures." That is, a known weight of tin is heated to a known temperature and then dropped into a known weight of water, also at a known temperature. From the rise in the temperature of the water we calculate the heat given off by 1 gm. of tin in cooling 1° C.—the specific heat.

Apparatus.—The calorimeter arrangement of Exp. 9, with a 200-cc. beaker instead of the 400-cc. beaker there recommended; a delicate thermometer graduated in 0.1°. For heating the tin, a large test-tube (25×180 mm.) is suspended in an Erlenmeyer flask as seen in Fig. 16, the latter serving as a steam jacket. To prevent the test-tube from dropping down too far in the flask, a filter paper is folded about it and tied in place as indicated. This also serves to catch any drops of water which might run off into the calorimeter when the tin is poured out. For taking the temperature of the tin a common, but accurate, thermometer will be needed.
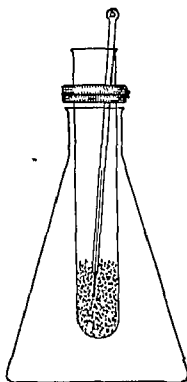
Procedure.—Weigh the calorimeter beaker, put into it 100 cc. of water, and weigh again. Now place this in the graniteware cup with proper insulation, and then suspend within it the tenth-degree thermometer. (To prevent breakage it will be well to suspend the thermometer by means of a strong cord, not by means of a clamp, which is likely to slip.) After stirring the water for a few minutes by means of the thermometer, the bulb of which should be *entirely immersed*, take the temperature as accurately as possible. This should be done by means of a lens, and the thermometer should be tapped gently with a pencil just before reading. Avoid parallax.

Now weigh out on the laboratory balance about 100 gm. of granulated tin (of about 30-mesh size) and place it in the test-tube for heating.

Fig. 16.

30

Put about 1 inch of water in the Erlenmeyer, embed the thermometer in the tin, plug the mouth of the test-tube loosely with cotton, and then suspend it in the flask as seen in the sketch. Finally heat the water to rapid boiling.

When the temperature of the tin has reached its maximum (about 99°), read the thermometer in the calorimeter once more, withdraw the thermometer from the test-tube, remove the cotton, and instantly pour the tin into the calorimeter, tapping the tube to insure complete removal. Now stir with the thermometer until the temperature of the mixture is uniform (perhaps 30 sec.), taking care to stir the tin as well as the water. Finally read the thermometer accurately, as at first.

You now have all the necessary data. Calculate first the water equivalent of the calorimeter and add this to the weight of the water, calculate next the change in the temperature of the water and calorimeter, and then the number of calories of heat absorbed by them. This heat all came from the tin in cooling through a considerable number of degrees. Find what has been the total change in the temperature of the tin, and then calculate the number of calories it gave off in changing one degree. Finally calculate the heat liberated by 1 gm. of tin in cooling one degree. This is its specific heat.

Now proceed with the calculation of the atomic weight of tin as follows:

(1) Apply Dulong and Petit's law for the determination of the approximate atomic weight.

(2) Calculate the equivalent weight of tin from the following data: 9.8137 gm. of tin were oxidized to stannic oxide. The weight of the oxide was 12.4598 gm.

(3) Compare the equivalent weight with the approximate atomic weight, and thus determine what multiple of the equivalent weight to use for the exact atomic weight. Calculate then the exact atomic weight.

CHAPTER VII

VALENCE

Exp. 17. Valence of Sodium, Magnesium, and Aluminum.

This group of experiments is intended to direct attention to the simple idea that valence is measured by the combining or displacing capacity which an element has towards hydrogen. Weights of metals are taken which are exactly proportional to their atomic weights. This insures the presence of the same number of atoms of each metal. We allow these metals to react with an excess of water or hydrochloric acid until entirely consumed. The volume of hydrogen obtained in each case is a measure of the number of atoms displaced, and therefore of the valence. We also note that the relation here found is the same as the relation between the atomic weights and the equivalent weights.

Apparatus.—As seen in Fig. 17. The flask should not be larger than 200 cc., but the neck should be large enough to take a No. 4 two-hole rubber stopper.
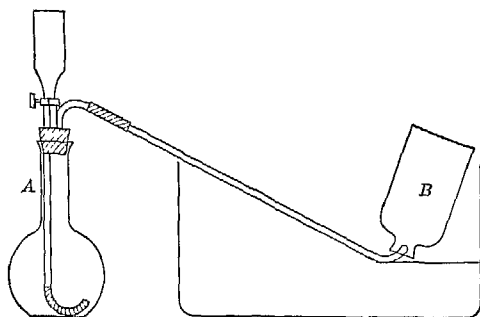
Fig 17.

The tap funnel holds 60–75 cc. and has a stem small enough to pass through the stopper easily when wet. Be sure that the stop-cock does not leak, lubricating if necessary.

The outlet tube must not project below the stopper, or hydrogen will be caught beside it and cannot be removed.

The piece of rubber tubing at the end of the funnel tube is intended to prevent hydrogen going up the tube and being trapped there. It should not kink so as to close the tube.

Sodium, one of the metals used, must be protected while being weighed. This is done by enclosing it in a gelatin capsule. Use size No. 1; a larger size would permit the use of too large a piece of sodium, and make the experiment dangerous.

Procedure A. Sodium.—First fill the pneumatic trough and place the bottle for the collection of hydrogen. Next weigh the gelatin capsule accurately, place within it a single, cleanly cut piece of sodium as large as possible (instructor), and then cover and weigh as before. When ready, place the loaded capsule under the mouth of the bottle, and allow it to rise to the surface of the water inside. Within about ten minutes the capsule will dissolve and allow the sodium to react with the water. When the reaction begins it is well to throw a towel over the bottle, so that in case of a possible small explosion no harm can be done. When the reaction is over, adjust levels, stopper the bottle, and then proceed in the usual way to measure the hydrogen. Finally calculate its volume down to standard conditions, not forgetting to allow for water vapor.

Also calculate from your data the equivalent weight of sodium.

Procedure B. Magnesium.—First calculate what part of an atomic weight of sodium you used in Procedure A, and then calculate what weight of magnesium will represent the same fraction of its atomic weight. To get exactly this weight of the metal, carefully clean a piece of the wire of exact known length (10 cm.) with emery cloth, and then weigh. It is then only the matter of a moment to calculate the length necessary to give the proper weight. The wire should be straight, of course, when measured, and the ends should be cut off square. The cutting can best be done by rolling under the edge of a knife. If this work is carefully done no after weighing is necessary.

Fill the flask *A* full of water, drop in the magnesium wire, and push the stopper with the connecting tubes in place. Now run water through the apparatus from the tap funnel until *all* the air is removed from the neck of the flask and from the delivery tube, but close the cock while there is still a very little water above it; that is, do not allow air to get in.

Now put the bottle *B* in place, and run perhaps 30 cc. of concentrated hydrochloric acid into the flask, taking care not to let any air in. After the magnesium is completely dissolved, drive over the last of the hydrogen by running water through the apparatus as at first. Finally measure the mixture of hydrogen and water vapor, and calculate the volume of the latter down to 0° and 760 mm.

Calculate also the equivalent weight of magnesium.

How many equivalent weights does the atomic weight of magnesium contain?

Assuming that the volume of hydrogen obtained in the case of sodium represents " one atom," how many atoms of hydrogen does a like atomic proportion of magnesium displace?

Procedure C. Aluminum.—Using the same apparatus and proceeding in the same way as in B, obtain the same data for aluminum. It may be necessary to heat the flask to start the reaction. The water should not be boiled, however.

How many equivalent weights does the atomic weight of aluminum contain?

How many " atoms " of hydrogen do you get, as compared with the case of sodium?

When all the data for the three metals have been obtained, arrange in tabular form as follows:

	Na.	Mg.	Al.
(1) Weight of metal used			
(2) Fraction of an atomic weight.			
(3) Volume of hydrogen at 0° and 760 mm.			
(4) Relative volumes (vol. with sodium = 1)			
(5) Valence, from relative volumes.			
(6) Equivalent weights			
(7) Atomic weight.			
(8) Number of equivalents in at. wt.			
(9) Valence, from (8).			

Exp. 18. Oxidation and Reduction Valence.

The following experiments are intended to show how we determine the active valence of oxidizing and reducing agents. We shall make up solutions containing 1/10 mole * of each compound per liter. We shall then have present in each case the same number of molecules per cubic centimeter. If, then 1 cc. of solution A reacts with 1 cc. of solution B, we know that 1 molecule of substance A reacts with 1 molecule of substance B; and, that, therefore, the active valence of A and B are equal, one as an oxidizer, the other as a reducer. If 1 cc. of solution A reacts with 5 cc. of solution B, we know that 1 molecule of A reacts with 5 molecules of B; and this shows that the valence of A is five times that of B.

We shall use as our standard a solution of iodine. The active valence of iodine as an oxidizing agent is 1. This is shown by the fact that the neutral, uncombined iodine, I, as seen in its brown or violet solutions changes to the colorless ion I^- when it goes into combination, to form, for example, HI or KI. The fact that the charge becomes negative indicates that iodine is an oxidizing agent.

The standard iodine solution will be furnished. Directions for preparing the other solutions are included.

Apparatus.—The ordinary volumetric apparatus, including one burette with glass stopper, one burette with rubber tip, a set of five pipettes, and one or two graduated flasks.

* 1/10 atomic weight in the case of elements.

In using the volumetric apparatus, the following suggestions should be followed:

(1) The inside of the glass should be so clean that drops will not form on the sides when the solutions are run out.   (Why?)

(2) The stop-cock of the burette should be slightly lubricated to prevent setting and leakage.

(3) The Mohr burette should be provided with a glass tip, such as is used on a wash bottle, and with a pinch clamp.

(4) When in use, burettes should be clamped so as to stand perfectly plumb.   Nothing more certainly distinguishes the slovenly worker than a carelessly placed burette.

(5) If a standard solution is to be placed in a wet burette, the latter must first be rinsed with a little of the solution.   Otherwise the solution would be diluted, or contaminated with some other solution.   Do not forget the part below the stop-cock.

(6) Before beginning a titration, remove any bubbles of air from the tip of the burette.

(7) Avoid parallax in reading a burette.

(8) Do not put oxidizing agents (e.g., $KMnO_4$) in rubber-tipped burettes.

(9) Pipettes are calibrated to deliver the amount marked upon them without rinsing.   After allowing a pipette to drain about 10 sec., remove the drop at the tip by closing the top with the finger and then warming the bulb with the hand.   Do not blow through a pipette.

Procedure A.   Reducing Valence of Sodium Thiosulphate.—In making up the solution of thiosulphate two students may work together,* preparing 500 cc.

Proceed as follows: Calculate the molar weight of the hydrated salt $Na_2S_2O_3 \cdot 5H_2O$, and from this calculate the amount necessary for 500 cc. M/10.   Select clear crystals of thiosulphate—those which have not lost any water of hydration—crush in a mortar, and then weigh out (as above) the calculated amount.   Dissolve in a small amount of water and make up to 500 cc. in a graduated flask.   *Do not forget to mix well after making up to volume.*

Now fill one burette with the iodine solution and the other with the thiosulphate, first reading over *all* the precautions about the use of burettes.   Run off into a beaker 25 cc. of the iodine solution and drop the thiosulphate solution into this with constant stirring until the color of the iodine is just discharged.   To make sure of the end point, titrate back with a drop or two of the iodine solution until a faint color remains

* Students work in groups only on the preparation of the solutions, not in any case on the subsequent titrations.

after stirring, and then discharge again with thiosulphate. Finally take both the readings accurately, estimating to 0.1 of a division.

The end point will be much sharper if a solution of starch paste (note 1) is added just before the end point is reached. Use about 5 cc. of the solution made up as directed. The iodine forms a bright blue solution with the starch, thus making it possible to detect a much smaller amount of iodine than could be detected by means of its own color. The starch paste solution should not be added, however, until the end point is almost reached (note 2). It is always best to use starch in iodine titrations, and in some cases, e.g., with highly colored solutions, it is absolutely necessary.

Now reread the introduction given at the head of this series of procedures, and then decide as to the active valence of thiosulphate as a reducing agent. Also explain the above method.

NOTES.—(1) Take a piece of starch the size of a pea, moisten with cold water, and then stir in very slowly about 50 cc. of boiling water. This solution must be used fresh

• (2) If the starch is added when there is still a large amount of iodine present, the granules will become so deeply impregnated with it that it is not easily removed at the end.

Procedure B. The Oxidizing Valence of Potassium Permanganate. —Four students work together on the preparation of the solution. One hundred cc. will be enough. Obtain a graduated flask for the purpose.

Calculate the weight of 1/10 mole of permanganate, $KMnO_4$, and take 1/10 of the calculated amount for 100 cc. Since the amount to be weighed here is small, it will be best to use the accurate balance, but there is no necessity for weighing beyond the second place. (What per cent error would 0.01 gm. make on 1.5 gm.?) When the proper amount is weighed out, dissolve in about 20 cc. of hot water, and then transfer to the graduated flask. There will be some difficulty in telling when all the solid is dissolved, on account of the opaqueness of the solution. The particles may usually be felt, however, with a rod (note 1), and if the solution is carefully decanted into the graduate flask, any such particles may then be seen. When the salt is all in solution, bring the volume up to the mark with water and then *mix carefully*.

To determine the oxidizing valence of permanganate, measure out carefully with a pipette 10 cc. of the M/10 solution into a beaker. To this add, *first*, 5 cc. of 6 N sulphuric acid, and *second*, 20 cc. of a 10 per cent solution of potassium iodide (note 2). Dilute now to about 100 cc. and then titrate the iodine with thiosulphate as directed under procedure A, excepting that you leave the iodine solution where it is in the beaker and titrate it all (note 3). Be very careful not to overstep the end. If

you do, however, it will be possible to tell what excess of thiosulphate has been added by titrating back with the standard iodine solution.

When through with the titration, decide as to the oxidizing valence of the permanganate, and explain carefully the steps in the above method.

Notes.—(1) Do not use a rubber-tipped rod. Permanganate is decomposed by rubber or any organic matter.

(2) The amount of potassium iodide is considerably in excess of the amount required in the reaction, but the excess is needed as a solvent for the iodine which is set free

(3) Be very sure that you know exactly what is the purpose of all these reagents, and also just what is taking place at all times. Do not begin the experiment until you do know these things. Is it necessary that the potassium iodide and the acid be accurately measured?

Procedure C. The Reducing Valence of Ferrous Iron.—As a carrier for ferrous iron, we shall use the stable and definite salt, ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, each mole of which contains one atomic weight of iron.

Four students working together may prepare 500 cc. of the ferrous iron solution as follows: Calculate the weight of 1/10 mole of the iron-carrying salt (this will give also 1/10 mole of iron) and take half the calculated amount for 500 cc. Dissolve in about 200 cc. of water containing about 5 cc. of concentrated sulphuric acid (note 1), and then make up to volume and mix.

Take 50 cc. of the ferrous iron solution (measured with a pipette), add 5 cc. of 6 N sulphuric acid (note 2) and titrate (note 3) with the permanganate until a point is reached where a faint pink color remains after thorough stirring.

Knowing the oxidizing valence of the permanganate, you can now calculate the reducing valence of ferrous iron.

Notes.—(1) If the salt is dissolved in pure water, the iron in it is slightly oxidized by the dissolved air; and since oxidation demands an increase in the amount of the negative radical, the only thing which can happen is for OH from the water to unite with the iron to make up the deficiency. This forms a basic sulphate insoluble in water, and the solution thus becomes turbid. In presence of the acid no basic sulphate can be formed, and besides, permanganate titrations must be carried out in acid solution.

(2) $KMnO_4$ has a different valence, in neutral solution.

(3) Do not use a rubber-tipped burette.

Procedure D. The Oxidizing Valence of Potassium Dichromate.—Four students working together prepare 100 cc. of M/10 dichromate, $K_2Cr_2O_7$. To do this, calculate the molar weight, and then proceed to weigh out 1/100 of this amount for 100 cc. M/10.

Place in a beaker 10 cc. of 10 per cent solution of potassium iodide and 5 cc. of 6 N sulphuric acid, add *exactly* 5 cc. of the standard dichromate, and, after stirring, titrate the iodine with thiosulphate. Because of the green color of the Cr^{+++} it will be necessary to use starch indicator but this should not be added until the iodine is nearly all titrated, when the red color gives place to a greenish yellow. When the starch is first added the color will probably be very dark green, almost black; but as the titration proceeds this color will change to a rich blue; and when the end point is reached the blue will give place to the light chromium green.

The relative volumes of dichromate and thiosulphate furnish the means of calculating the oxidizing valence of the dichromate. Having made this calculation, explain also the steps in the above method.

Exp. 19. Zinc as a Reducing Agent.

Iron is commonly determined volumetrically by reducing it to the ferrous condition and then titrating with a standard oxidizer, such as dichromate or permanganate. When gotten into solution from its ores or alloys iron is usually either all ferric or a mixture of ferrous and ferric

To get it all into the ferrous condition, one or the other of two common reducing agents is used: these are stannous chloride or zinc. When metallic zinc acts as a reducer the change occurring is,

$$2Fe^{+++} + Zn \rightarrow Zn^{++} + 2Fe^{++}$$
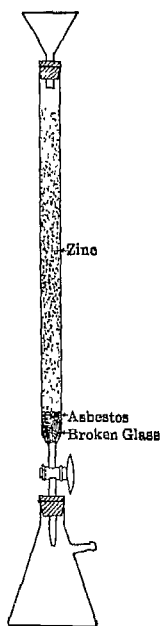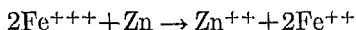
There are several methods of using zinc as a reducing agent, but the one which is probably the best employs the apparatus known as the " Jones reductor " (Fig. 18), the preparation and use of which will be described.

The tube is 50 cm. long, including the tip below the stop-cock, and 2 cm. in diameter. When in use it is supported by a ring stand. The zinc used is 30 mesh or slightly larger, and to avoid needless waste is amalgamated. The process of amalgamation is conducted as follows: Dissolve 2 gm. of pure mercury in 10 cc. of 1 : 1 nitric acid, dilute to 200 cc. in a large flask, add the zinc (200 gm.) and shake for two minutes. Pour off the solution, wash the zinc thoroughly and then transfer to the reductor. To use the reductor proceed as follows: Turn on the suction and pass through the tube 100 cc. of 2 per cent (by volume) sulphuric acid. Close the cock while there is still some acid in the funnel (note 1). Discard this acid, and again pass through the tube 100 cc. of 2 per cent

Fig 18.

acid, stopping as before. Test this acid with a drop of permanganate to see if it contains any oxidizable substance, (Fe^{++} or H_2O_2). A single drop should color it permanently; if it does not, repeat the washing.

Now take the iron solution to be tested, add to it about 2 per cent (by volume) of sulphuric acid, heat to 60° C., and pass through the reductor, at a rate not to exceed 50 cc. per minute. Follow, without allowing air to enter, with 150 cc. of 2 per cent acid (previously prepared), and then with 75 cc. of water, leaving a small amount of the latter in the funnel. The iron is now ready for titration and the reductor is ready for the next determination (provided this determination is carried out the same day). Titrate the iron solution immediately in the suction flask.

Procedure.—To show the quantitative action of the reductor, take 50 cc. of the ferrous iron solution of Exp. 18, add 5 cc. of 6 N sulphuric acid, titrate carefully with the permanganate, recording the amount of the latter used, and then pass the solution of ferric iron through the reductor, as explained above, and titrate again. The amount of permanganate used in both titrations should be exactly the same (note 2).

NOTES.—(1) If air is allowed to enter the apparatus, H_2O_2 will be formed, and this reduces permanganate.

(2) If the ferrous salt contained a trace of ferric the amount of permanganate used in the second titration will slightly exceed that used in the first.

CHAPTER VIII

SOLUBILITY AND SUPERSATURATION: CONCENTRATION

Exp. 20. Supersaturated Solutions of the Hydrates of Sodium Sulphate.

Apparatus.—A Büchner funnel (9 cm.) set up according to Fig. 19. This funnel has a perforated bottom over which a filter paper is placed. It is always used with suction, like a Gooch crucible, and is thus a great time-saver when large volumes of liquids are to be filtered.
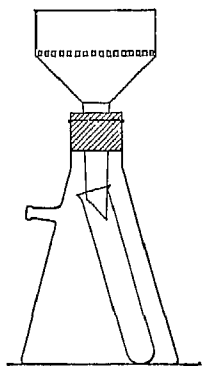
If the volume of liquid is small it is well to receive it in a large test-tube placed inside the suction flask.

Procedure.—Place 25 gm. of anhydrous sodium sulphate in a casserole, add 40 cc. of water, and heat gently, stirring constantly with a thermometer, until the temperature reaches about 40° C. Maintain this temperature until most of the salt dissolves, and any possible traces of the hydrated phases are destroyed. The small amount of powdered material left over is the anhydrous salt. (Would this dissolve if the temperature were raised?)

Fig. 19.

Filter immediately on a Büchner, making sure beforehand that the apparatus is perfectly free from any traces of the hydrated salts, or any salt, in fact. When this is done, return the solution to the casserole (carefully rinsed) and again heat to 40° C. (not higher). This temperature insures absolute freedom from either hydrate. (Why?) Now transfer the solution to a small flask which has been freshly rinsed with distilled water, pouring the solution in through a clean funnel, and taking great care not to get a trace on the neck or sides of the flask. Now immediately stopper the flask with a wad of *clean* cotton, and then set it in an ice-box, or any place where the temperature is about 10° C. Be careful not to shake the flask in moving it.

If the experiment is successful, the solution will, after a time, deposit a compact mass of heptahydrate crystals. When the process is finished the solution is in equilibrium with the heptahydrate, but is strongly supersaturated with respect to the decahydrate. The latter fact may

be shown by dropping in a minute crystal of the latter salt. When this is done crystallization will begin all over again. Note, however, how different is the shape of the new crystals which are formed.

Explain each part of the procedure in this experiment. This is best done by drawing the solubility curves, and making them the basis of your reasoning.

Exp. 21. The Test for Potassium.

Apparatus.—A test-tube rack and 10 test-tubes.

Procedure.—Dissolve 10 gm. of tartaric acid and 10 gm. of potassium nitrate each in 50 cc. of water, and filter the two solutions. Place a row of 10 test-tubes on the rack, and add to each 5 cc. of the tartaric acid solution. Now, to tube No. 1, add 1 drop of the potassium nitrate solution, to No. 2 add 2 drops, to No. 3, 3 drops, etc. Gently shake each tube to mix the contents. Is a precipitate formed in any case? With a glass rod, scratch the inside of each tube, beginning with No. 1, and after a few minutes, notice whether anything has occurred. If you are in doubt about some of the tubes inoculate the contents with a minute drop from No. 10. In which tubes were the solutions supersaturated?

Would you consider this a fairly delicate test for potassium? Under what conditions might the test fail?

Exp. 22. Normal Solutions of Hydrochloric Nitric and Sulphuric Acids.

Apparatus.—An accurate hydrometer having a range of 1–1.2. A tall cylinder to use with the hydrometer. A 50-cc. volumetric flask, accurately calibrated. This apparatus is calibrated to be correct at 15° C. (60° F.), and is not to be relied upon at any other temperature.

Procedure.—We shall first determine the density of the somewhat diluted acids, using two different methods. We can then find from the accompanying table, the actual amount of acid present per cubic centimeter, and by a simple calculation can determine the amount needed for 500 cc. or 1 liter of normal concentration. The diluted acids are used because the concentrated acids are much less convenient to work with. A convenient dilution is about 6 N. Concentrated hydrochloric acid, is about 12 N, concentrated nitric about 16 N, and concentrated sulphuric about 36 N. To prepare the 6 N acids we need, therefore, to dilute 6 cc. of hydrochloric to 12 cc., 6 cc. of nitric to 16 cc., and 6 cc. of sulphuric to 36 cc., or larger amounts in like proportions.*

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* These acids may be made up in large amounts for the class, and kept where the temperature does not rise above 15° C.

It is understood, of course, that acids made up by specific gravity, as outlined above, will be accurate only within about 1 per cent; but the method has the advantage of being quick and easy, and for many purposes is accurate enough. When necessity arises we shall use a more accurate method.

Determine the density by both of the following methods, two or three students working together:

(a) Take enough of one of the 6 N acids to fill the hydrometer cylinder within about 5 cm. of the top, adjust the temperature to 15° C. *before placing in the cylinder*, and then measure the density as accurately as possible by means of the hydrometer. The readings obtained by all the groups working during the same period will be posted on the blackboard, and the average of all these readings will be used as the most probable value.

(b) Clean and dry the volumetric flask, using the methods of Exp. 10, note 1. Having done this, weigh the flask to the second decimal place only. Now again adjust the temperature of the acid to 15° C., and then fill the flask with it at this temperature, taking care that the lower edge of the meniscus comes exactly on the mark, and that there are no drops clinging to the glass above. Weigh the flask and contents as directed in the case of the empty flask. The difference between these two weights constitutes what is usually termed the "apparent weight," or, "weight in air," of the acid. The true weight, or weight in vacuum would be slightly greater. Thus, on an object having a density of 1.1 this vacuum correction is 0.00095 gm. per gram apparent weight; where the density is 1.2, this correction is 0.00086 gm. per gram apparent weight.* Having made the vacuum correction and thus obtained the true weight, you have the data for calculating the density, which is the weight of 1 cc. The readings obtained by this method will be posted as under (a), and the average value used by all the class.

You now have two average values for the density of one acid obtained as above, and may take for your working value the mean of these two. All the class will then be using the same value, and must, of course, obtain the same results.

Now, knowing the density of the acid, consult the following tables and determine the weight of actual acid per cubic centimeter at the determined density. Values lying between those given must be found by interpolation:

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* For a wider range of values, see Findlay, Practical Physical Chemistry, p. 29 (1915).

Hydrochloric Acid at 15° C.		Nitric Acid at 15° C.	
Density.	Grams per cc.	Density	Grams per cc.
1.070	0 152	1.155	0.296
1.075	0 163	1.160	0.306
1.080	0.174	1.165	0.316
1.085	0.186	1.170	0.326
1.090	0 197	1.175	Q.336
1.095	0.209	1.180	0.347
1.100	0 220	1.185	0.357
1.105	0.232	1 190	0.367
1 110	0.243	1.195	0.378
1 115	0 255	1 200	0.388

Sulphuric Acid at 15° C.	
Density.	Grams per cc.
1 155	0 248
1.160	0.257
1.165	0.266
1.170	0 275
1.175	0.283
1.180	0.293
1.185	0 301
1.190	0.310
1.195	0.319
1.200	0.328

Having determined the weight of acid per cubic centimeter, calculate the number of cubic centimeters required for 500 cc. of normal concentration, measure out the amount (still at 15° C.) into a graduated flask, using a burette which has been carefully rinsed with the acid, and make up to the mark with distilled water. Mix by inverting several times—this is *very* important.

When the calculation has been made as to the number of cubic centimeters of 6 N acid required, it is a wise precaution to have the result checked by the instructor before measuring out the acid.

After one acid has been made up, determine the density of the other two by the same method, and then make up 500 cc. of each to normal concentration. Do not forget the precautions about temperature, etc. In determining the density by method (*b*) it will not be necessary to dry

out the flask and weigh again.   Simply rinse with a small amount of the acid you intend to use, and then fill and weigh.

Any unused 6 N acid may be returned to the stock bottles, but care should be taken not to mix the different acids.

The normal acids are to be placed in the 600-cc. bottles of the outfit and kept for future use.

Exp. 23. Normal Sodium Hydroxide.

Calculate the weight of actual NaOH required for 600 cc. normal alkali, then weigh out 10 per cent more than this to allow for water in the sticks, dissolve in water, and make up to volume.   *Mix well*, as directed under 22.

Since the amount of water in the sticks is not accurately known, you must determine the actual concentration of this solution by com- parison with one of the acids.   To do this fill one of the burettes (the rubber-tipped one) with the alkali, and the other with the normal HCl, not forgetting the proper precautions about the use of burettes.   Now run off about 25 cc. of the acid into a beaker; add 2 drops of methyl orange indicator, and then titrate with the alkali to the first appearance of a permanent yellow color.   Titrate back with the acid to the appear- ance of a faint pink.   The true end point is a combination of pink and yellow—a salmon color—which may be obtained by touching off from the burette tip a fraction of a drop of either solution, as required. When the titration is done, carefully take the burette readings.   The amount of base used should be less than that of the acid, indicating that it is more concentrated.   The readings may be like this: NaOH 23.2 cc., HCl 25.3 cc.   This indicates that the alkali is more concentrated than the acid in the proportion of 25.3 : 23.2.   To be reduced to the same concentration as that of the acid it must be diluted in just the proportion indicated by these figures.   Calculate from your figures to what volume 500 cc. of alkali must be diluted, and then measure out 500 cc. in a graduated flask, transfer to the 600-cc. bottle, and make up to proper volume by adding water from a pipette or burette.   Mix well as directed above, and then check by retitrating against the acid.   It should cor- respond exactly.

When the sodium hydroxide is made to correspond with one of the acids as above, check the other two acids by titrating against it. They may differ by as much as 0.2 cc. on 25 cc.

The solution of sodium hydroxide should be kept in a bottle with a *rubber* stopper; a glass stopper will soon become hopelessly set.

CHAPTER IX

FREEZING-POINTS AND BOILING-POINTS OF SOLUTIONS: OSMOTIC PRESSURE

Exp. 24. Molecular Lowering of the Freezing-point of Water.

Apparatus.—A thermometer graduated in 0.1° and having the range −10 to +50°; a strong test-tube, 25×180 mm.; a larger tube to serve as a jacket; an aluminum stirrer; a small battery jar (4×4 in.) to serve as a cooling bath. The apparatus is assembled as seen in Fig. 20, the jacket tube being supported by a ring stand, which also holds the battery jar:

Procedure.—Make up a solution of ethyl alcohol containing 1 mole of actual C_2H_5OH in 1000 gm. of *water*. Use the so-called "absolute alcohol" of 99.9 per cent purity, and make up not to exceed 100 cc. of the solution. Since alcohol is a volatile liquid and also likely to absorb moisture from the air, the best procedure for weighing will probably be first to weigh accurately (to the second place) a small stoppered flask which has previously been thoroughly dried, then measure into it by means of a dry pipette 5 cc. of the alcohol, and weigh again. Knowing

Fig. 20.

the weight of the alcohol, it is an easy matter to calculate what weight of water must be added to give the proportions above mentioned. Having made this calculation, add to the alcohol the proper amount of water, and *mix thoroughly*.

Prepare a freezing bath by mixing finely crushed ice and water, and then adding enough common salt to lower the temperature to −6° C. Place in the battery jar such a quantity of the mixture that, when the jacket is immersed about 3 in. deep, the jar is nearly full.

First determine the freezing-point of water alone (note 1), proceeding as follows: Place about 20 cc. of water in the inner tube, insert the thermometer and stirrer as shown in the sketch, and then cool by insert-

ing directly in the bath, stirring constantly.   When the temperature has fallen to about $-1°$ or $-2°$, stir vigorously to induce freezing (note 2). When ice begins to separate, place the tube in the jacket and stir gently for a moment until the temperature becomes constant; then read the thermometer with a lens, tapping gently, and estimating to 0.01°.   Be sure that numerous ice crystals are floating about in the liquid when the reading is taken, or the temperature may not be the freezing-point at all (note 3).   Now remove the inner tube, thaw the ice by holding the tube in the hand for a moment, and then repeat the determination. At least five readings should be taken in this way.   If these do not differ by more than 0.03°, the average may be taken as the freezing-point of the water.
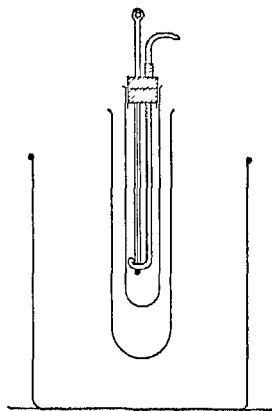
Determine the freezing-point of the alcohol solution as follows: Remove the water from the inner tube, rinse the latter with the alcohol solution, and then add about 20 cc. of the same.   Cool in the bath as above, until a temperature of $-4°$ or $-5°$ is reached, and then to induce freezing inoculate with a fragment of clean ice the size of a wheat grain. Remove the tube from the bath, and stir until the amount of ice has diminished somewhat (note 4), then place in the jacket, and after stirring a moment, read the temperature.   Do not forget that you are reading downward from the zero, and that, therefore, the hundredths are to be estimated downwards from the nearest division above the end of the mercury thread.   Thaw the ice and repeat as above, obtaining five concordant readings.   Take the average of these as the freezing-point of the solution.

The molecular lowering for water is the difference between the freezing-point of the pure water and that of the solution.   Calculate this.

NOTES —(1) Water freezes at zero, of course; but the thermometer may not be correct.

(2) Pure water tends to become supercooled without freezing just as a solution becomes supersaturated without depositing crystals, and the same means have to be taken to prevent this condition.

(3) If no ice is present the temperature may be either above or below the freezing-point.   If numerous ice crystals are present and the water is kept stirred so as to bring these rapidly into contact with all parts of the liquid, the temperature will remain at the freezing-point until all the water has solidified.   Abstraction of heat does not change the temperature but simply hastens the change of state.   The same sort of thing is true when the ice is melting; the change of state here absorbs heat, so if the amount of ice is fairly large and good contact between ice and water is kept up by stirring, the temperature remains at 0°.   Too rapid heating, with too small an amount of ice present may result in raising the temperature above 0°.   It is merely a case of equilibrium between the rates at which heat can be delivered and absorbed.

(4) When a non-saturated solution freezes, ice alone separates.   This makes the solution more concentrated and thus makes the freezing-point lowering greater than

is expected. We are, therefore, careful not to have too large an amount of ice separated at the time we take the reading. However, the amount must not be reduced to a few minute crystals, or the temperature may rise above the freezing-point.

Exp. 25. Molecular Weight of Propyl Alcohol.

Apparatus.—Same as that of Exp. 24.

Procedure.—Make up a solution containing propyl alcohol in some known amount, say 100 gm., per 1000 gm. of water. Ten gm. dissolved in 100 gm. of water will be enough. Determine the freezing-point of the solution exactly as directed in Exp. 24. If Exp. 24 has not been performed it will be necessary to carry out the first part here also, namely, the determination of the freezing-point of the pure water on the thermometer you are using. The molecular lowering for water, 1.86°, may be used in the calculation below without determination.

When the freezing-point of water and that of the solution have been determined, calculate from your data what weight of propyl alcohol would have been necessary to give the molecular lowering; this is its molecular weight. The formula for propyl alcohol is C_3H_7OH. How nearly correct is your value?

Exp. 26. Qualitative Experiment on Osmotic Pressure.

Apparatus.—A diffusion thimble of parchment paper A Fig. 21; a glass adapter B of the proper size to fit the thimble after the latter has been thoroughly soaked in boiling water; a capillary tube 3 or 4 feet long, 1-mm. bore C. Prepare the apparatus as follows: Fill the thimble with water, immerse in a beaker of water and boil until expanded and free from air; then draw over the end of the adapter and tie securely in place with waxed thread. When not in use the thimble and adapter should be kept in water to prevent drying out.

Procedure.—Prepare a concentrated solution of cane sugar. Fill the thimble by pouring the solution through a slender funnel. The rubber connector should be in place, and this should be filled also. Finally, holding the apparatus by the adapter, push into connection with the capillary tube. Some of the solution will, of course, be forced a short distance up the tube, but this does no harm. Suspend the thimble now in a cylinder of water as shown in the sketch. If the apparatus is tight and properly set

Fig. 21.

up, the solution should ascend the tube at the rate of about half a centimeter per minute.
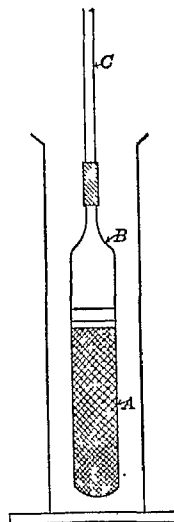
CHAPTER X

THE THEORY OF IONIZATION

Exp. 27. Salt Effect.

Procedure A. Salt Effect with Acetic Acid.—To 300 cc. of distilled water add 6 drops of methyl orange indicator, stir thoroughly, and then remove 100 cc. to another beaker. To the remaining 200 cc. now add sufficient N acetic acid to give the characteristic salmon color of the end point (about 3 drops). After stirring thoroughly, divide into two equal parts. To one of these portions containing the acetic acid add about 10 gm. of pure, neutral sodium chloride. Stir until solution is complete, and then place alongside the second acidulated portion for comparison. Is there any evidence of greater ionization, resulting in stronger acidity?

To prove that the change is not due to any action of the salt on the indicator itself, add a similar amount of the sodium chloride to the portion containing the indicator alone. If the salt is really neutral there should be no change in color.

Show why water causes acetic acid to ionize and why sodium chloride enhances the effect.

Procedure B. Salt Effect with Ammonium Hydroxide.—To 50 cc. of a M/5 solution of magnesium sulphate add 10 cc. of N ammonium hydroxide, stir, and let stand for five minutes. Some of the magnesium will be precipitated as the hydroxide, $Mg(OH)_2$, by the hydroxyl ion from the base; but, due to slight ionization of the latter (note 1) the precipitation is not complete. Anything that will increase the ionization of the ammonium hydroxide will cause further precipitation of the magnesium. To show that sodium chloride does this, filter the solution on a Büchner funnel, and then, to the clear filtrate, add about 10 gm. of pure, neutral salt. Explain the result.

NOTE.—(1) The ammonium salt formed in the reaction also suppresses the ionization of the ammonium hydroxide, but this in no way interferes with the accuracy of the experiment.

Exp. 28. Degree of Ionization from Abnormal Freezing-point Lowering.

Apparatus.—Same as that used in Exp. 24.

Procedure.—Make up about 100 cc. of a solution of sodium chloride

containing the salt at the rate of 1 mole in 1000 gm. of water. Determine the freezing-point lowering as in the case of propyl alcohol, obtaining five values as there directed.

When the data have been obtained, the degree of ionization may be calculated as follows: Let α equal the fraction ionized (the degree of ionization), and let n equal the number of ions resulting from the dissociation of 1 molecule. Also let d equal the observed molecular lowering. Now if the breaking up of 1 molecule produces n ions, we obtain in the case of this 1 molecule $n-1$ particles more than we had to begin with. If α is the fraction of molecules ionized, the total number of particles added by this process will be α $(n-1)$; and if 1 equals the number of molecules before any are broken up, then the total number of particles now present will be $1+\alpha$ $(n-1)$. Finally, since the freezing-point lowering is proportional to the number of particles present, no matter what their size, the observed lowering will be related to the true molecular lowering $(1.86°)$ just as the total number of particles is related to the original number. This may be expressed thus:

$$d : 1.86 :: 1+\alpha(n-1) : 1$$

From this we obtain

$$\alpha = \frac{d-1.86}{1.86 \ (n-1)}$$

Substitute your data in this formula, and calculate the degree of ionization of the salt you used (note 1).

NOTE.—(1) The value will be somewhat too large on account of the hydration of the ions.

Exp. 29. Ionization and Chemical Tests.

Procedure A. Ionization and Speed of Displacement of Hydrogen.—Take three test-tubes: fill No. 1 two-thirds full of N hydrochloric acid, No. 2 with N phosphoric acid (note 1), and No. 3 with N acetic (note 2). Take three pieces of pure sheet zinc (1 cm. ×2 cm.) and wrap each neatly in a small piece of brass gauze (note 3). Having done this, drop them into the test-tubes, and after waiting for the reaction to get well under way, note the relative speeds. The reaction, as you know, consists in the displacement of hydrogen by zinc. Consult the table of ionization, and note whether the speeds are proportional to the degrees of ionization of the individual acids.

Procedure B. Ionization of Iron Salts and Iron Complexes.—Treat a solution of ferric chloride with a few drops of a solution of ammonium or potassium thiocyanate. Repeat the same test, using potassium ferri-

cyanide as the carrier of ferric iron.   Explain the difference between the two tests.

To one 5-cc. portion of potassium ferric-oxalate solution add ammonium thiocyanate, and to another add sodium hydroxide.   Why do you obtain a test for ferric ion in one case and not in the other?

Procedure C. Chloride and Chlorate Ion.—To 5 cc. each of solutions of sodium chloride and potassium chlorate add a few drops of silver nitrate solution.   Explain the results.

Procedure D. Ionization of Boric Acid.—Test a solution of boric acid with a drop of methyl orange.   Is enough H^+ ion present to affect the indicator?   Why?

Procedure E. Ionization of Mercury Salts.—To separate 5-cc. portions of mercuric chloride and mercuric nitrate solutions add a solution of potassium dichromate.   Look up the degrees of ionization of these two salts of mercury, and then decide whether the tests obtained are in accord with the ionization data.

NOTES.—(1) Phosphoric acid acts practically like a monobasic acid, the secondary and tertiary ionization being so slight.   " Normal " may, therefore, be taken to mean " molar," if methyl orange indicator is used in making it up.   This acid is best made up by the specific gravity method of Exp. 22.   The concentrated acid has a density of 1.7, and contains 85 per cent actual H_3PO_4.

(2) Glacial acetic acid is approximately 100 per cent pure, and the density is 1.055.   The normal acid is best made up in this case, also, by the method of Exp 22.

(3) Pure zinc reacts very slowly with an acid.   With the gauze the zinc forms an electric couple, causing the reaction to proceed smoothly, but still in proportion to the ionization of the several acids.

Exp. 30. Ionization and Catalysis.

Procedure A. Acid Catalysis.—Take four 100-cc. flasks and place in each 40 cc. of water.   To the four in order then add an accurate 10-cc. portion of one of the following acids, viz., N HCl, N HNO_3, N H_2SO_4, and N H_3PO_4 (note 1).   That is, add HCl to No. 1, HNO_3 to No. 2, etc.   Now to each flask add exactly 2 cc. of methyl acetate, and mix the contents thoroughly by closing with a cork and shaking.   Let the reaction proceed for fifteen hours (*not longer*).

In the meantime, measure out with the same pipette 10-cc. portions of each of the above acids, and determine by titration the exact number of cubic centimeters of N NaOH required to neutralize them, using phenolphthalein as indicator (note 2).

At the end of the fifteen hours, add to each flask from a burette the proper amount of N NaOH to neutralize the acid originally added; and then, using phenolphthalein indicator, titrate the acetic acid produced by the hydrolysis in each case.   On account of the excess of methyl acetate always present here, the end-point color of the indicator

will not remain long after the titration is finished.   (Explain in light of Procedure B.)   Take as the end of the titration the point where a faint pink color remains for ten seconds after stirring.

Remember that the number of cubic centimeters of alkali used represent quantities of acetic acid, and that quantities of acetic acid represent the speeds of the hydrolytic reactions.   With this in mind, arrange the several numbers of cubic centimeters in descending order, placing them in column 2 of the table following.   In column 1 write the names of the corresponding catalyzing acids, and in column 3, the degree of ionization of these acids as obtained from the table in the text.

Catalyzing Acids	Cc. of N H ac Produced	Ionization of the Catalyzing Acids.

Do you note a direct proportionality between ionization and catalysis? (note 3).

Procedure B. Basic Catalysis.—Into each of two beakers put 50 cc. of water and 1 drop of phenolphthalein.   Then add to one beaker 1 cc. of N NaOH and to the other 1 cc. of N NH₄OH.   Finally add to each (to the ammonia first), 2 cc. of methyl acetate, quickly mix by stirring, and note the time.   The acetic acid generated by the reaction neutralizes the alkali, and thus removes the color of the indicator.   The time required is inversely proportional to the ionization of the alkali in the two cases.

NOTES.—(1) This is really molar phosphoric acid; that is, normal to methyl orange.

(2) Phenolphthalein is used here because it must be used later in titrating the acetic acid set free in the reaction.   With this indicator phosphoric acid will act as a dibasic acid, and so will appear to be of 2 N concentration.

(3) The hydrogen ion is not used up in the process of catalysis, but the methyl acetate is.   For this reason the reaction tends to slow down as it proceeds, and finally come to a standstill.   This effect is less noticeable in the case of a weak acid, where the reaction is slow, because the amount of acetate remains nearly constant.   Hence the final result will probably be somewhat to the advantage of the weaker acids. In other words, it will make the weaker acids appear a little stronger than they are.

Exp. 31. Heat of Neutralization.

Apparatus.—The calorimeter apparatus used in the determination of specific heat. The beaker should hold not more than 300 cc., allowing complete submersion of the thermometer bulb when the beaker contains 200 cc. of liquid. The thermometer should be graduated to 0.1° and should have a range of 0°–50°.

The water equivalent of the calorimeter may be calculated from its weight; but since only part of the beaker will be heated, and since the bulb of the thermometer is not thus included, a better method is the following:

Place 100 cc. of water in the calorimeter and take its temperature accurately. Take another 100 cc. of water and warm it to a temperature about 8° higher, and take its temperature accurately with the same thermometer. Next pour this second portion of water into the calorimeter. Proceed then to measure the temperature of the mixture, but first cool the thermometer bulb back to its original temperature by immersing in another beaker of water, such as was first put in the calorimeter. The mixture should be thoroughly stirred before the temperature is read. The rise in the temperature of the cold water, multiplied by 100, will be the heat received by it. The fall in temperature of the warm water, multiplied by 100 will be the heat lost by it. The difference between these products will be the heat received by the calorimeter and thermometer. This amount, divided by the change in temperature of the apparatus will be the water equivalent of the latter in grams.

Procedure.—First prepare N/2 solutions of NaOH, HCl and NHO₃ by diluting the normal solutions already on hand. Proceed then to determine the heat of neutralization of the *two acids* as follows: Measure out exactly 100 cc. of the NaOH and of one of the acids and place in 150 cc. beakers of *tall* form. Set these on a clean porcelain tile, and suspend above them the thermometer in such a position that it reaches almost to the bottom of either beaker. Measure the temperature of the two solutions very accurately, tapping the thermometer and waiting until the reading is constant. Use a lens. In transferring the thermometer from one solution to the other, remove the adhering drop by touching the bulb to the side of the beaker. Record the average of the two temperatures. Now set the tile, carrying the two beakers, to one side, and put in its place the calorimeter, adjusting the thermometer so that it almost touches the bottom of the beaker. Finally, pour the two solutions together into the calorimeter and stir with the thermometer. For reading the temperature make use of the following scheme:

Note the exact time when the two solutions are mixed, and at the

end of exactly one minute begin a series of readings taken one minute apart and lasting until the rate of fall becomes constant. Plot the values on coordinate paper, and obtain the true maximum temperature by extrapolation. An example will make this clear: The temperature before mixing was, in a certain case, 23.45°. Beginning one minute after mixing, the readings were 26.48, 26.53, 26.48, 26.44, 26.40, and 26.36. These values are seen plotted in Fig. 22.

From *A* to *B* the slope of the curve is constant; that is, the fall in temperature is the same per minute. If this curve is extended back (extrapolated) to the Y-axis, it marks the temperature which really ex-
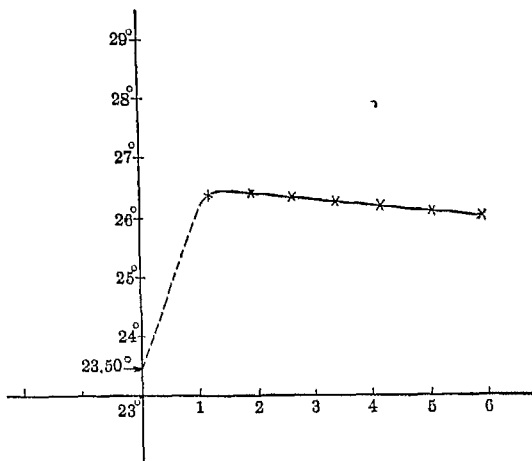
FIG. 22.

isted at the moment of mixing, and which would have been indicated later by the thermometer if no heat had been lost by radiation. This temperature is 26.61°. The real rise then, due to the neutralization, was 26.61 − 23.45°, or 3.16°.

When the final temperature has been read and the rise calculated by use of the above scheme, the total heat evolved is calculated in the usual way. The total volume of the solution is 200 cc. and since it is so dilute (N/4), it may be reckoned as 200 cc. of water. To this must be added the water equivalent of the calorimeter and thermometer bulb determined experimentally as directed above.

When the total amount of heat produced by the neutralization has been calculated, it must be remembered that only a fraction of an equivalent was taken. It then remains to calculate by proportion what amount of heat would have been produced if a whole equivalent weight of acid had been neutralized. This will be the heat of neutralization. It should not differ from 13,700 cal. by more than 200 cal. in the case of either acid.

Explain fully the significance of this experiment.

CHAPTER XI

INDICATORS

Exp. 32. Sensitiveness of Methyl Orange Indicator and its End-point Correction.

Apparatus.—Ten Nessler's tubes, 100 cc.; a color comparator as seen in Fig. 23. The lower bar A of the comparator is double, and between the two parts is a diaphragm of colorless celluloid upon which the Nessler's tubes rest. The light is reflected up through the tubes from the white enameled surface of the slanting board B. When in use, the comparator is placed so as to face a large window. Artificial light can scarcely be used for color work, excepting, possibly, the so-called "daylight lamps."
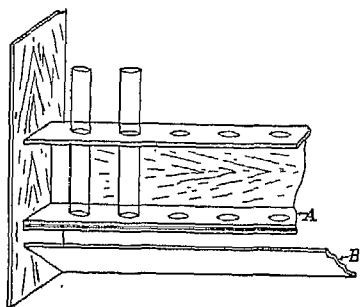
Fig. 23.

Be sure that the Nessler's tubes are clean and free from the least *trace* of acid or alkali. The Nessler's tubes must not be set up on an open desk; they should always be placed in the comparator to avoid breakage.

Procedure.—Starting with your normal hydrochloric acid, prepare 1 liter of N/1000 acid. Place seven of the tubes in the comparator. Beginning then at one end of the row, add in succession to the tubes the following amounts of the N/1000 acid: 70 cc., 60 cc., 50 cc., 40 cc., 30 cc., 20 cc., 10 cc. Having done this, fill the tubes with distilled water to the 100-cc. mark. Before going further with the experiment calculate the concentration of the acid in each tube and state it both as a decimal and in terms of the minus powers of 10. Also submit your values to the instructor for verification.

To each tube now add two drops of methyl orange indicator * and then stir the contents thoroughly by closing with the hand and inverting.

* 0.1 gm. of the solid in 100 cc. of water is the usual concentration.

54

Notice which concentration gives the salmon color commonly recognized as the end point for this indicator.   Notice also that in the more dilute solutions the concentration of the H^+ ion is too small to affect the indicator, making it appear as though the solution were neutral, which it is not.

At the dilutions here used, we are safe in saying that the acid is all ionized in each case.   If this is so, then the total concentrations, as you worked them out above, represent also the concentrations of the hydrogen ion.   Place these concentrations in a horizontal row, labeling them (H^+), meaning "hydrogen ion concentration."   Work out the corresponding hydroxyl ion concentration in each case and place these below the others.   They should be labeled (OH^-).   In testing the accuracy of these latter values you have only to notice whether the product $(H^+) \times (OH^-)$ in any case is 10^{-14}.

What concentration of H^+ and OH^- are present in a solution which gives the end-point color with methyl orange?   Check this point under the proper concentrations by means of an arrow, $\uparrow$, and label it " methyl orange end point."

End-point Correction.—Suppose you were titrating a solution of hydrochloric acid in a volume of 200 cc.; when the end point is reached, what weight of HCl remains unneutralized?   What part of 1 cc. of N HCl does this amount represent?

If you placed 50 cc. of N HCl in a beaker, diluted it to 400 cc. and then titrated to the methyl orange end point with NaOH, what per cent of the acid would remain unneutralized?   To state it otherwise, what would be the percentage error in the titration?

What fraction of 1 cc. of N/10 HCl will be required to give the methyl orange end point in a volume of 500 cc.?   If, then, in a certain titration we used 49.72 cc. of N/10 HCl and the total volume of the solution is 500 cc., what volume of the acid was actually used in the neutralization?

Exp. 33. Sensitiveness of Phenolphthalein Indicator.

Apparatus.—Same as in Exp. 32.

Procedure.—Dilute 1 cc. of N sodium hydroxide to 10 cc. and then dilute 1 cc. of this solution to 1000 cc., preparing thus a solution of alkali having a concentration of 0.0001.   Place seven Nessler's tubes on the comparator, and add to them in succession the following amounts of the above solution: 100 cc., 90 cc., 80 cc., 70 cc., 60 cc., 50 cc., and 40 cc. Having done this, fill the tubes to the 100-cc. mark with distilled water.

Assuming now that all the NaOH is ionized, work out for each tube

the concentration of OH⁻ and H⁺, and record, as directed in Exp. 32, in terms of the minus powers of 10.

To determine which of these concentrations of H⁺ and OH⁻ produces the first suggestion of a pink color (the "end point") with phenolphthalein, add to each tube two drops of the indicator solution,* and mix by closing with the hand and inverting (note 1). Check this point under the proper concentrations as directed in 32, and label it " Phenolphthalein End Point " (note 2).

NOTES.—(1) Be very sure that there is no trace of acid or alkali on the hand here. Such a trace might amount to more than the alkalinity of the extremely dilute solutions with which you are working.

(2) The value obtained by this simple dilution method will not be so nearly correct as in the case of methyl orange. This is due to the fact that a considerable proportion of the alkali in such an extremely dilute solution is neutralized by the carbonic acid (from the air) always present in distilled water. This makes the color change of the indicator appear to come where the OH⁻ concentration is greater than it really is. The true value is (OH^-) 10^{-6} and (H^+) 10^{-8}.

Exp. 34. Choice of an Indicator. †

Procedure A. Titration of a Weak Acid.—Measure out with a pipette 10 cc. of N acetic acid, and titrate with N sodium hydroxide, using methyl orange as indicator. Does the end point appear when the amounts of acid and base are equal? Repeat the titration with another portion of acid, using phenolphthalein as indicator. Explain the results.

Procedure B. Titration of a Weak Base.—Measure out 10-cc. portions of N ammonium hydroxide, dilute to about 50 cc. to reduce the volatility, and then titrate with N hydrochloric acid, using in one case methyl orange and in the other case phenolphthalein, as indicator. Explain the results.

Note that one of the indicators used above was especially sensitive to OH⁻ ion, the other to H⁺ ion. Can you make a general statement as to the kind of indicator necessary, (a) with weak acids? (b) with weak bases?

Consult the indicator table below and select two indicators which you think would take the place of the two used above for the same titrations.

* A 1 per cent solution in alcohol.

† Complete understanding of this subject involves the matter of ionic equilibrium. Under that head further study will be undertaken.

Indicators.	Colors Exhibited.			End-point Concentrations	
	In Acid	End Point.	in Alkali	(H^+).	(OH^-).
Dimethylamino-azo benzene	decided pink	salmon	yellow	4.9×10^{-4}	2×10^{-11}
Methyl orange	pink	salmon	yellow	2.1×10^{-4}	4.8×10^{-1}
Cochineal	orange	pink	lilac	1.7×10^{-4}	6×10^{-11}
Sodium alizarin sulphonate	brass yellow	brown	cherry red	$5 2 \times 10^{-5}$	1.9×10^{-10}
Congo red	blue	violet	red	5.2×10^{-5}	$1 9 \times 10^{-10}$
Alizarin	brass yellow	old rose	pink	3.7×10^{-5}	2.7×10^{-10}
Methyl red	violet red	pink	yellow	1.2×10^{-5}	$8 5 \times 10^{-10}$
Azolitmin (litmus)	red	violet	blue	10^{-6}	10^{-8}
Neutral red	magenta	pink	yellow	10^{-7}	10^{-7}
Rosolic acid	yellow	rose	pink	1.4×10^{-8}	7×10^{-7}
Phenolphthalein	colorless	pink	magenta	$9 2 \times 10^{-9}$	1.1×10^{-6}
Thymolphthalein	colorless	sky blue	blue	5.9×10^{-10}	1.7×10^{-5}
Trinitrobenzene	colorless	yellow	orange	10^{-13}	10^{-1}

Exp. 35. Titration of Polybasic Acids.

Procedure A. Phosphoric Acid.—Take 10 cc. of approximately molar phosphoric acid, and titrate with N sodium hydroxide, using methyl orange as indicator. What does the basicity of phosphoric acid seem to be with this indicator? Explain.

Repeat the titration with another 10 cc., using phenolphthalein as indicator. Show why phosphoric acid appears to be dibasic in this case. Since the secondary hydrogen ion does not redden methyl orange, its concentration must be below a certain value. What value? Since phenolphthalein remains colorless in presence of this same secondary hydrogen ion the concentration of this ion must be above a certain value. What value?

Titrate a third 10-cc. portion of the phosphoric acid with the alkali, using trinitrobenzene as indicator. Explain the result.

Procedure B. Carbonic Acid.—Carbonic acid is an example of a very weak dibasic acid. Its primary ionization is too weak for methyl orange but strong enough for phenolphthalein. Its secondary ionization is too weak even for the latter indicator. For the primary ionization we have

$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$
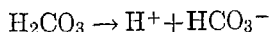
When this primary hydrogen is neutralized, phenolphthalein shows the pink color with the next drop of NaOH, and we then have in solution the

bicarbonate ion, HCO_3^-, such as would be found in a solution of sodium bicarbonate, $NaHCO_3$. This may be seen by preparing a clear solution of sodium bicarbonate, and adding to it a drop of phenolphthalein indicator. The solution will be found either to give the pink color of the end point, or to be ready to do so upon the addition of a drop of normal alkali.

A solution of sodium carbonate (Na_2CO_3) is alkaline to both methyl orange and phenolphthalein. If we titrate this with an acid, we have the changes mentioned above occurring in reverse order. We have the $CO_3^=$ gradually combining with the H^+ ion from the acid to form HCO_3^-, thus:

$$CO_3^= + H^+ \rightarrow HCO_3^-$$
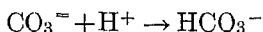
When this change is completed the color due to the phenolphthalein vanishes. Notice that this end point comes when the two equivalents of carbonate have reacted with one equivalent of acid. If we now add methyl orange and continue the titration, the pink color of this indicator will not appear until the other equivalent is titrated; for, as the acid is added, the bicarbonate ion is first changed to the very slightly ionized carbonic acid, which does not affect the indicator, thus:

$$HCO_3^- + H^+ \rightarrow H_2CO_3$$
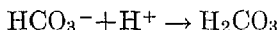
With phenolphthalein, therefore, sodium carbonate acts like a univalent or mon-acid base, while with methyl orange it acts like a bivalent or di-acid base. Since this salt can easily be obtained pure and dry it is much used as a standard in making up standard acid solutions.

Weigh out 1 gm. of pure, anhydrous sodium carbonate, Na_2CO_3, dissolve in about 100 cc. of *cold* water, add phenolphthalein, and titrate *slowly* (note 1) with N hydrochloric acid. The end point will be a little obscure, but if the titration is carried out over a white tile and is pushed a little to the extreme, the result will be exact. When this end point is reached, add methyl orange and proceed to the final end point. Record the amount of acid used from the beginning up to each end point, that is, from 0 to end 1, and from 0 to end 2. How are these two amounts related?

NOTE.—(1) The water should be cold to prevent the escape of CO_2. Also, if the titration is too rapid the reaction may go through both steps locally and CO_2 may escape instead of forming HCO_3^-, as above indicated.

CHAPTER XII

HOMOGENEOUS EQUILIBRIUM

Exp. 36. Speed of Reaction and Speed Constant.

We shall catalyze the hydrolysis of methyl acetate by means of hydrochloric acid, and shall try to show that the speed of the reaction is proportional to the concentrations of both the methyl acetate and the hydrogen ion   We shall also calculate the speed constant, K_1, for the forward half of the reaction

$$CH_3COOCH_3 + H_2O + H^+ \rightleftarrows CH_3COOH + CH_3OH + H^+$$
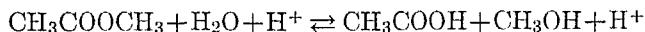
The equation makes it appear as if the speed of the reaction should also be proportional to the concentration of the water present, and it is; but we shall arrange to have the concentration of the water practically the same in all our trials, thus canceling out this factor so far as relative speed is concerned.

Procedure.—You have on hand approximately normal solutions of NaOH and HCl, which, if made according to directions (Exp. 23), correspond exactly cubic centimeter per cubic centimeter when methyl orange is used as indicator.   But, on account of the presence of carbonate, this may not be the case if phenolphthalein is used.   Therefore, since phenolphthalein must be used later in titrating the acetic acid formed in the reaction, you must know the relative strength of the acid and base as shown by this indicator.   To do this, measure out 10 cc. of the acid and titrate with the NaOH, using a drop of phenolphthalein indicator.   Be very exact about this.

Fit four 150-cc. flasks with good corks, and then charge according to the following table.   For measuring the acid use a 10-cc. pipette, and for the methyl acetate a 2-cc. (dry) pipette.   Add the water to all the flasks first, then the acid, and finally the acetate.   Proceed with the last rapidly, but take care not to let the end of the pipette enter the mixture so as to transfer this to the stock of methyl acetate.

59

Flask No.	Cc. Water	Cc N HCl.	Cc. Me ac.
1	48	10	2
2	38	20	2
3	46	10	4
4	36	20	4

As soon as the ingredients are added, stopper the flasks tightly with wet corks (note 1), and shake thoroughly to mix the contents. Let the reactions proceed for *just* two hours.

At the end of this time add quickly, in 1–4 order, sodium hydroxide in amounts equal to the acid originally used. This stops the reaction. Now immediately titrate the acetic acid formed in the hydrolysis, using phenolphthalein as indicator. The end point will not be permanent, because an excess of methyl acetate will be present. Take as the end of the titration the point where a faint pink color remains for 10 seconds after thorough stirring. The number of cubic centimeters of NaOH used in each case may be regarded as cubic centimeters of acetic acid, and is, therefore, a measure of the speed of reaction (note 2).

It will be noted that the total volume in each flask is 60 cc. Therefore, in flasks 1 and 3, the acid becomes $N/6$ and in 2 and 4 it becomes $N/3$ when mixed with the water. $N/6$ HCl is 91 per cent ionized, and $N/3$ is 88 per cent. Calculate the hydrogen ion concentrations, (H^+), in each.

The concentrations of methyl acetate may be stated simply in terms of the cubic centimeters used.

Now post the data in tabular form as below, and work out the values indicated:

Flask No.	(H^+).	(CH_3COOCH_3)	Relative Speed Calculated	Cc. NaOH (=speed)	Relative Speed Observed.	K_1.
1		2				
2		2				
3		4				
4		4				

As indicated in the development of the equilibrium law, the relative speeds may be calculated on the assumption that they are proportional to the concentrations of one or both of the reacting substances. That is, we may let the relative speed be 1 in the first case; and if in the second

:ase the H^+ concentration is 1.93 times as great, while that of the acetate remains constant, we may assume that the relative speed will here be 1.93, etc.

The observed relative speeds may be calculated from the amounts of NaOH used, letting the first amount be 1, as above.

K_1 shows the relation between the concentration product of the reacting substances and the speed. It is the same factor as that similarly represented in the general equation, $(A) \times (B) \times K_1 = S_1$, and is worked out in the same way. (CH_3COOCH_3) goes in place of (A), (H^+) in place of (B), and cubic centimeters of NaOH in place of S_1. The value worked out from these units will probably be about 11 for this reaction, depending on the temperature.

NOTES —(1) Wet corks will not absorb the methyl acetate.

(2) Speeds are usually stated in moles per minute or hour; here we are stating them in cubic centimeters of acid formed in two hours. Values obtained by different people for the same case will probably differ somewhat because the temperatures used will probably not be quite the same. This does not count against the accuracy of any one set of values obtained by a single person, for all the flasks used should certainly be at the same temperature.

Exp. 37. Equilibrium Constant.

Note that in 36 we were not determining the equilibrium constant K, but simply the speed constant K_1 for the forward reaction $CH_3COOCH_3 + H_2O + H^+ \rightleftarrows CH_3COOH + CH_3OH + H^+$. To obtain K we should first need to determine K_2 for the reverse reaction. K would be the ratio between the two constants; thus $K = K_2 / K_1$.

A simpler way to determine the equilibrium constant for the hydrolysis of methyl acetate would be to allow the reaction to proceed until equilibrium had been established; that is, until the speeds of the forward and reverse actions were equal. We should then have the equilibrium relations indicated by the equation

$$\frac{(\text{Me ac}) \times (H_2O) \times (H^+)}{(\text{MeOH}) \times (\text{H ac}) \times (H^+)} = K$$

It is evident that, since all these substances exist in the same solution, the factor (H^+) will be the same for both numerator and denominator, and will, therefore, cancel out. We should then have

$$\frac{(\text{Me ac}) \times (H_2O)}{(\text{Me OH}) \times (\text{H ac})} = K$$

The value for K would be found, then, by simply determining the concentrations of the several factors which are in equilibrium as represented in the equation, and then solving in the usual way.

We shall carry out the experiment in two ways: first, by mixing known amounts of the constituents represented in the numerator of the equilibrium equation, and allowing the reaction to proceed until equilibrium is established; and second, by mixing known amounts of the constituents represented in the denominator, and allowing equilibrium to be reached from this side. The concentrations should so adjust themselves that the value for K will be the same in the two cases.

Procedure.—Take two dry flasks of 150-cc. capacity, fitted with tight corks, and number them 1 and 2.

In flask No. 1 place 10 cc. of methyl acetate and 2 cc. of water, each measured accurately with pipettes.

In flask No. 2 place 10 cc. of glacial acetic acid and 5 cc. of methyl alcohol.

Place in each flask as a catalyzer, 1 cc. of N HCl. This virtually adds to each flask 1 cc. of water which must be allowed for later in the calculation.

Stopper the flasks loosely, and clamp them on a ring stand in such a position that the bottoms only are immersed in water contained in a large graniteware bath. Heat the water in the bath to 50°, and maintain it thus for three hours. This heating simply hastens the reactions towards their equilibrium points. When the heating is well begun and no further pressure is likely to be developed, the corks should be inserted more tightly to prevent leakage. After thus heating, let the flasks stand where they are until the next afternoon.

At the end of this time, add to each flask 1 cc. of normal NaOH to neutralize the HCl previously added, and then proceed to titrate the acetic acid as in Exp. 36, using phenolphthalein as indicator and taking the proper precautions about the end point.

Having titrated the acetic acid and recorded the values, proceed with the calculations as follows:

Flask No. 1

Remembering that 1 liter of normal alkali represents 1 mole, calculate what fraction of a mole of acetic acid was present. This represents the factor (H ac) in the equation above. The fraction of a mole of alcohol formed will be the same as this, representing the factor (MeOH). To obtain the value for the unhydrolyzed acetate, first find the weight used by multiplying its volume (10 cc.) into its density (0.964). From this calculate the mole fraction used. The mole fraction still left (Me ac) equals this minus the mole fraction of acetic acid or alcohol formed. To get the factor (H_2O) find the initial mole fraction of

water present, and subtract from this the mole fraction of acetic acid formed.

Substitute these values in the equilibrium equation, and solve for K.

Flask No. 2

The titration value for acetic acid converted into the fraction of a mole represents the factor (H ac). The initial molar concentration of acetic acid is found by first getting the weight of acid used (the density is 1.055) and then converting to a mole fraction. The initial molar concentration minus the factor (H ac) represents the fraction of a mole transformed into acetate, and therefore stands for the factor (Me ac). The initial concentration of the alcohol is found in the same way (density 0.796), and this minus the factor (Me ac) represents the present concentration, or mole fraction, (MeOH). The factor (H_2O) will be the initial concentration plus the factor (Me ac).

These values are to be substituted in the same equation as those from flask No. 1, and the value for K is to be worked out in the same way.

Note the significant fact that, despite the wide difference in the concentrations of the reacting substances, the ratio K really has a nearly constant value.

Exp. 38. Ionic Equilibrium of Cupric Bromide.

The following experiment is intended to illustrate the general methods of displacing ionic equilibrium.

Procedure.—Weigh out on the laboratory balance 6 gm. of cupric bromide, $CuBr_2$. Note the color of this substance in the solid state. Place in a small beaker and dissolve in 15 cc. of water. Cupric ions, Cu^{++} are blue in color, bromide ions, Br^-, are colorless, and the non-ionized cupric bromide is black. To what extent would you say, then, that this salt is ionized as you now have it in solution? Write the equilibrium equation for the ionization of cupric bromide.

Take 5 cc. of the concentrated solution, add water in 2-cc. portions, shaking after each addition, until 10 cc. have finally been added. Note and explain the successive changes in color.

Take another 5-cc. portion of the concentrated solution, and add an equal volume of water, obtaining an emerald-green solution. To this add about 2 gm. of sodium bromide. Explain the change in color. What is the general term applied to this method of displacing ionic equilibrium?

To the final portion of the concentrated solution add 2 gm. of pow-

dered cadmium nitrate, and stir until dissolved. We shall then have the following equilibria:

$$CuBr_2 \rightleftarrows Cu^{++} + 2Br^-$$

$$Cd(NO_3)_2 \rightleftarrows 2NO_3- + Cd^{++}$$
$$\Updownarrow \qquad\qquad \Updownarrow$$
$$Cu(NO_3)_2CdBr_2$$
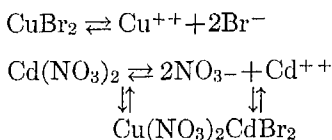
Cupric nitrate is highly ionized, so we shall not look for any disturbance of the equilibrium from that source. But cadmium bromide is only weakly ionized; therefore a considerable amount of the non-ionized salt will at once be formed, thus lowering the concentration of the bromide ion. What effect does this have upon the upper equilibrium? What effect on the concentration of the cupric ion, Cu^{++}, and the non-ionized cupric bromide, $CuBr_2$? What evidence do you have that your explanations are correct? What name is applied to this method of displacing ionic equilibrium?

Exp. 39. Common Ion Effect with Acetic Acid and Ammonium Hydroxide.

Procedure A.—From the ionization table (text) find the degree of ionization of molar acetic acid. From this calculate the concentrations of the ions and the non-ionized part, and then work out the ionization constant. Note that the ion product is practically equal to the ionization constant in this case. Would this be true in any other than a molar solution?

Measure out 50 cc. of molar acetic acid, and add to it enough sodium acetate $(NaC_2H_3O_2 \cdot 3H_2O)$ to make the concentration of this salt 0.2 molar (M/5), stirring until dissolved. Again referring to the ionization table, calculate the acetate ion concentration coming from the acetate, and then the total acetate ion concentration. Having done this, calculate the quantitative effect this increase of acetate ion must have on the hydrogen ion concentration which must still be in equilibrium with it. What color should methyl orange show in this solution? Test your calculation by adding a drop of the indicator and stirring.

What would be the effect of adding still more sodium acetate? What concentration of hydrogen ion would have been present in the above solution if enough sodium acetate had been added to make the concentration of this salt molar? (Molar sodium acetate is 53 per cent ionized.)

Procedure B.—Let us assume that our problem here is to calculate how much ammonium chloride must be added to 50 cc. of N/10 NH₄OH to reduce the OH^- ion concentration to the turning point for phenol-

phthalein. $(1.1\times10^{-6}.)$ Substitute values for N/10 ammonium hydroxide in the equilibrium equation

$$\frac{(NH_4{}^+)\times(OH^-)}{(NH_4OH)}=0.000018$$

and then calculate the value of the product

$$(NH_1{}^+)\times(OH^-)$$

Assuming that this product remains practically constant (prove this), calculate what total concentration of $NH_4{}^+$ ion will be necessary to reduce that of the OH^- to the desired value. You will find this concentration to be something like 1.7. To get this concentration of $NH_4{}^+$ you will need to use ammonium chloride of such a concentration that it will probably not be more than 70 per cent ionized (note 1). On the assumption that the salt is 70 per cent ionized, calculate the total concentration necessary to give the proper $NH_4{}^+$ concentration. Having done this, you can at once determine the number of grams of NH_4Cl necessary to give this concentration in 50 cc.

When you are sure that your value is correct, weigh out the proper amount of ammonium chloride, place in a small beaker, and dissolve in 50 cc. of N/10 ammonium hydroxide. Finally add a drop of the indicator. The color should be a barely perceptible pink—the end-point color.

NOTE.—3 N ammonium chloride is 68 per cent ionized, and therefore gives an $NH_4{}^+$ concentration of 2.04.

Exp. 40. Neutralization by Formation of a Non-ionized Acid or Base.

Procedure A.—Measure out 50 cc. of normal HCl into a beaker. What concentration of hydrogen ion is present in this solution? Add a drop of methyl orange and note the intense red color shown by the indicator. Now add to the solution sufficient sodium acetate to make the solution 1.8 molar with reference to this salt and stir until all is in solution. Note the effect on the indicator. What has become of the hydrogen ion? Suppose we consider the reaction as taking place in two steps: *first*, 1 mole of acetate reacting with 1 mole of acid; and *second*, the other 0.8 mole of acetate reacting. At the end of the first step, what concentration of hydrogen ion will be present? To what extent will the acid have been neutralized? Calculate the quantitative effect of the other 0.8 mole of acetate on the hydrogen ion concentration by the method employed in Exp. 39, counting the salt as 40 per cent ionized. What concentration of hydrogen ion should be present? Does this

account for the color shown by the indicator? What indicator would practically show its end-point color in this solution? Test your conclusion if the indicator is available. The test may be made in presence of the methyl orange.

Procedure B.—This procedure should refer to the neutralization of some strong base, say sodium hydroxide, by the addition of the salt of a weak base. This problem is left for the student to work out, with the suggestion that $N/10$ sodium hydroxide be used to start with, and that it be the problem to calculate what weight of NH_4Cl must be added to 50 cc. to reduce the OH^- concentration to the turning point for thymolphthalein (1.7×10^{-5}). The calculation is best made in two steps, as was done with acetic acid in Procedure A. This should afterwards be tested by experiment, of course. In order to see the very faint blue color of the indicator at its turning point, it may be necessary to compare the solution side by side with pure water.

Exp. 41. Hydrolysis of Salts.

Procedure A. Qualitative.—Test solutions of the following salts with red and blue litmus solution, and note whether the reaction is neutral, acid, or alkaline: sodium acetate, potassium carbonate, aluminum chloride, sodium chloride, ammonium chloride.

It may be necessary in some cases to compare the solution containing the indicator with pure water containing the indicator alone. If this is necessary place the two solutions in clean test-tubes and look down through them as you hold them side by side over a piece of white paper.

Write the proper equilibria, and explain each case carefully. Make some estimate also as to the relative degrees of hydrolysis in the different cases.

Procedure B. The Degree of Hydrolysis of Aniline Sulphate.—Aniline sulphate is the salt of a weak base, aniline hydroxide, and the strong acid, sulphuric. Its solution will, therefore, show an accumulation of H^+ ion. Our problem will be to measure the concentration of this H^+ ion, and from this to calculate the degree of hydrolysis.

The color comparator and six Nessler's tubes will be needed.

Prepare 1 liter of $N/1000$ hydrochloric acid, and then make up five standard tubes containing, respectively, 100 cc., 80 cc., 60 cc., 40 cc., and 20 cc., of this acid, filling each to the 100 cc. mark with distilled water. Prepare also 100 cc. of $N/10$ aniline sulphate solution (equivalent weight 142), and place in the sixth Nessler's tube. The temperature of this solution should be approximately 25° C. The tube containing it should be labeled to prevent confusing with the others. Arrange the tubes in the comparator so that the alternate holes will be left vacant.

Now add to each tube four drops of methyl orange indicator, and mix in the usual way. Having done this, match colors between the aniline sulphate solution and the acid solutions, and from the data thus obtained determine, as accurately as possible, the hydrogen ion concentration resulting from hydrolysis.

The calculation of the degree of hydrolysis may be made as follows: (a) First calculate the theoretical degree from the known constants. It has been shown in the classroom discussion of hydrolysis that in a case like this the following relation holds:

$$\text{(1)} \qquad \frac{(\text{total salt} - x)\,\alpha_1}{(\text{strong acid})\,\alpha_2\,(\text{weak base})} = \frac{K_{\text{base}}}{K_w}$$

where α_1 and α_2 are the degrees of ionization of the salt and strong acid respectively, where K_{base} is the ionization constant for the weak base, and x is the concentration of strong acid or weak base formed. It is evident without discussion that the left-hand member of this equation may go into the form

$$\frac{(\text{total salt} - x)\alpha_1}{x^2 \alpha_2}$$

It has also been shown that where the value of K_{base} is not smaller than 10^{-10} the degree of hydrolysis will be small, and that in such a case the concentration (total salt $-x$) may be taken as equal to (total salt). Such is the case with aniline sulphate, for K_{base} here is 5×10^{-10}. We shall, therefore, write the equation

$$\text{(2)} \qquad \frac{(\text{total salt})\alpha_1}{x^2\alpha_2} = \frac{K_{\text{base}}}{K_w}$$

The necessary constants are as follows:

(Total salt) = 0.1 (Normal conc.).
α_1 = 0.7 (Ionization of N/10 An_2SO_4).
α_2 = 0.61 (Ionization of N/10 H_2SO_4) (note 1).
K_{base} = 5×10^{-10}
K_w = 10^{-14}

Substitute these values in equation (2) and work out the value of x. This will be the concentration (weak base) or (strong acid). When it is remembered that each equivalent of salt hydrolyzed gives one equivalent of acid or base, the per cent hydrolyzed, or degree of hydrolysis, may be calculated at once.

(b) Note now that the H^+ ion concentration, as shown in (a), is 0.61 of the total concentration of acid (or base) formed. From the

hydrogen ion concentration which you have just determined experimentally, you may now calculate the *total* concentration of acid or base formed and then the per cent, or degree, of hydrolysis. The value thus obtained should agree well with the value calculated in (*a*).

NOTE.—(1) The concentration of the sulphuric acid formed is not N/10; but in the presence of the large concentration of the $SO_4^=$ ion from the salt, the degree may be considered the same as for an N/10 solution.

CHAPTER XIII

HETEROGENEOUS EQUILIBRIUM

Exp. 42. Decomposition of the Hydrates of Cupric Sulphate.

Select clear, blue crystals of the pentahydrate of cupric sulphate showing no efflorescence. Crush in a mortar, and weigh out a sample of 1 gm. into a crucible which has been previously weighed with its cover. Heat in an air bath at a temperature of 130° C. for forty-five minutes, cool in a desiccator, and weigh with cover in place. Repeat the heating to constant weight. Assuming that the original salt was the pentahydrate, calculate the number of molecules of water lost at 130° C. The calculation is as follows:

Let x = number of molecules of H_2O lost. The equation showing the decomposition will then be

$$CuSO_4 \cdot 5H_2O - xH_2O \rightarrow CuSO_4 \text{ aq.}$$
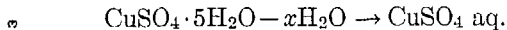
and

$$249.7 - 18x \rightarrow 159.6 + \text{aq.}$$

From this we obtain

$249.7 : 18x :: 1 :$ wt. of water lost: from which x. the number of molecules, may be calculated.

Why is it necessary to heat the pentahydrate to make it give off water? How could the same result be obtained without heating? What equilibrium conditions must be met in order to cause the hydrate left from the above reaction to lose its water? How can this be done? Would it require some definite temperature (assuming that the humidity of the air remains constant) or would any slight increase above 130° C. bring it about? Why? What if the humidity of the air became much less?

Test your conclusion by heating the hydrate left in the crucible to 200° C. for fifteen minutes. (The humidity of the air is not likely to have changed if this is done the same day.) After cooling in a desiccator, weigh. Explain the result.

Now heat to 250° for thirty minutes, cool and weigh. Finally heat to constant weight at this temperature. Now again substitute values in the equation above and calculate the total number of molecules of water lost at 250° C.

Exp. 43. Partition of Bromine between Water and Carbon Tetrachloride.

Apparatus.—Two 100-cc. glass-stoppered bottles. (Obtain from instructor.)

Procedure.—We shall take a solution of bromine in water and first determine its concentration. We shall then bring this solution in contact with carbon tetrachloride in two different proportions. The bromine will distribute itself between these two solvents according to the equilibrium law, which demands that the ratio between the concentrations in the two solvents shall be constant, although these concentrations may differ widely in the two cases.

Prepare a nearly saturated solution of bromine in water, or use the reagent "bromine water." Prepare also an approximately N/10 solution of sodium thiosulphate. (See Procedure A, Exp. 18, p. 35.)

To determine the concentration of the bromine water, remove 5 cc. with a pipette and transfer to a small Erlenmeyer flask containing 10 cc. of 10 per cent solution of potassium iodide. (This bromine solution should be transferred *directly* from the stock bottle to the potassium iodide solution *as directed*. It must not be carried in an open beaker or even placed in the flask *before* the potassium iodide solution is put in. If it is, bromine will be lost.) The iodine set free by the bromine is titrated with the thiosulphate. Repeat the determination, and record as the concentration of the bromine water the average number of cubic centimeters of thiosulphate required. All the concentrations we need to determine in this experiment will be stated in the same way: "cubic centimeters of thiosulphate equivalent to 5 cc. of solution."

Now place in one of the glass-stoppered bottles 5 cc. of carbon tetrachloride, measured very accurately with a dry pipette. In the other place 10 cc. of the same liquid. To each bottle add 50 cc. of the bromine water (pipette), and quickly insert the stoppers. Holding the stoppers in place, shake the bottles vigorously for ten minutes, and then let stand for half an hour for the two solvents to separate completely. At the end of this time remove a 5-cc. portion of the water layer from each bottle, and proceed as above to determine the concentration. Record these titrations as (Br_w). To get the concentrations in the other solvent proceed as follows: You have the titration for 5 cc. of the original bromine water. From this calculate the total value for 50 cc.; that is, all the bromine present in each case as cubic centimeters of thiosulphate. In the same way calculate the value for 50 cc. after partition in each case. The difference between the total bromine content before partition and after partition will be the bromine dissolved in the carbon tetrachloride layer, stated, of course, as "cubic centimeters of thiosulphate." Record, as the concentration of the bromine in the carbon tetrachloride, the

number of cubic centimeters thiosulphate equivalent to 5 cc. of this layer. This is designated as (Br_c).

After obtaining the two sets of values for (Br_w) and (Br_c), substitute in the equation

$$(Br_c)/(Br_w) = K$$

and calculate the values for K. They will be nearly identical if the temperature was the same in both bottles, and will not differ widely from 25.

Exp. 44. Partition of Succinic Acid between Water and Ether.

Apparatus.—Two 100-cc. glass-stoppered bottles, as in Exp. 43.

Procedure.—Place in bottle No. 1 about 20 cc. of a solution of succinic acid of about $M/10$ concentration. In bottle No. 2 place 10 cc. of the same solution, and then add about an equal volume of water. Now add to each bottle 20–25 cc. ether. Placing the stoppers in the bottles and holding them securely in place, shake the bottles vigorously for not less than five minutes to bring about the distribution of the succinic acid between the two solvents. When this has been done, let the two solutions stand a moment for the layers to separate, and then proceed to determine the concentrations in the several cases as follows:

By means of a dry 5-cc. pipette, remove a sample (5 cc.) of one of the upper layers (ether), place in a small Erlenmeyer flask, add about 50 cc. distilled water and a drop of phenolphthalein indicator, and then titrate *very carefully* with approximately $N/10$ NaOH (note).

Draw out 5 cc. of the lower layer in the same bottle and titrate in the same way. When the tip of the pipette is passing through the upper layer, this solution should be excluded by closing the upper end with the finger tip.

Having titrated the two layers, let the number of cubic centimeters of alkali used represent the concentration in each case, and then work out the partition ratio, C_{water}/C_{ether}.

Now proceed in the same way to determine the concentrations and the partition ratio for the solutions in the other bottle.

The ratios in the two cases should be almost exactly equal, although difference in temperature may cause them to differ slightly from those found by another worker.

NOTE.—This can be made up by dilution of the normal alkali. It is important that the titration be accurate, even though the alkali used be of unknown concentration: the *volumes* must be accurately known.

Exp. 45. The Cooling Curve of Sodium Sulphate in the Light of the Phase Rule.

Apparatus.—A large test-tube (25×180 mm.); a ring stand; two common thermometers; a 300-cc. beaker of tall form; a small reading

lens; a swab made by winding a little cotton around the end of a glass stirring rod.

Procedure A. (note 1.)—Take enough sodium sulphate decahydrate to make a layer in the test-tube about 7 cm. deep. Fasten the apparatus up on the ring stand, immersing the tube in water above the top of the sulphate. One thermometer measures the temperature of the water and the other that of the salt.

Heat the water to 45° C. and maintain this temperature until the sulphate has apparently melted down and the temperature of the inner thermometer reads nearly the same as the outer one. Both the water and the salt should be frequently stirred. During this process of heating the sulphate has given off its water of hydration, becoming anhydrous and in this water a part of the anhydrous salt has dissolved.

Now remove the beaker containing the water and wipe off the outside of the test-tube. The temperature will immediately begin to fall. Read the thermometer every *two* minutes until it has fallen to about 32.5°, using the lens and wiping off the inside of the tube with the swab if necessary. The transition from the anhydrous form to the decahydrate occurs at 32.4° C. (note 2), but the transformation may be suspended. To prevent this, drop in about 1 gm. (estimated) of decahydrate. From this time on take a reading every *ten* minutes, stirring well each time and, as far as possible, keeping the salt from sticking to the bottom of the tube. When the mass becomes very thick it will be best to stop stirring and simply leave the thermometer embedded in the middle of the tube. After the transition is complete and the temperature again begins to change, read every *five* minutes until the temperature nearly reaches that of the room.

All these readings should be recorded in the notebook thus:

Time.	Temperature.
2	45°
4	etc.
6	
etc.	
30	
40	
50	
etc.	

At the end of the experiment the values should be plotted on coordinate paper, and a *smooth*, neat time-temperature curve drawn.

Explain the shape of the curve in the light of the phase rule, as follows:

The system is made up of *two* components—What are they? At 45° C. there are three phases—What are they? What is the variance of a system having two components and three phases? How does the first part of the curve indicate this? At 32.4° C. another phase appears—What? We then have *four* phases and *two* components. What is the variance of such a system? How does the curve show this? When the transformation is complete one phase drops out—Which one?—and the system again becomes three-phase. What is the variance, and how does the curve show it?

Procedure B.—Proceed as in A, with one exception :. Do not stir the mixture after removal of the tube from the beaker of water. Be careful about this, even in reading the thermometer. It will be well, also, to have the mouth of the tube plugged with cotton.

You note, of course, that the transformation remains suspended, the fourth phase not appearing at all (note 3). The system therefore remains three-phase and univariant throughout. The data should be recorded and plotted as in A, when this will at once be seen.

When the temperature has dropped nearly to that of the room, it will be interesting to note what will happen if the fourth phase (the decahydrate) is introduced. To this end, drop in about a gram of the hydrate; then stir the mixture and proceed to read temperatures at ten-minute intervals. Plot and explain the data.

NOTES.—(1) This experiment will require a *full* laboratory period of three hours and a half.

(2) It may not be quite this by your thermometer, because the instrument may not be very accurate.

(3) The fourth phase may appear spontaneously. If it does it will only be necessary to stir and continue reading the temperatures as directed.

CHAPTER XIV

COMPLEX EQUILIBRIUM

Exp. 46. Precipitation and Solution of Silver Acetate.

Procedure A.—Calculate whether by the mixing of equal volumes of N/5 sodium acetate and N/10 silver nitrate a precipitate of silver acetate should be formed. Proceed as follows:

A saturated solution of silver acetate at 16° C. is 0.0603 molar, and the salt in this solution is 71 per cent ionized. Calculate the solubility product $(Ag^+) \times (ac^-)$ and the concentration of the non-ionized molecules (Ag ac).

When N/5 sodium acetate is mixed with N/10 silver nitrate the former becomes N/10 and the latter N/20. For the ionization of these salts at this concentration consult the Ionization Table in the text. Determine the concentrations of the silver ion and the acetate ion respectively.

Now, if a precipitate is to be formed, the ions must be able to unite in sufficient amount to *more* than saturate the solution with non-ionized molecules and still leave the ion product equal to the solubility product. If, then, x is the largest concentration of molecules that may be formed and still leave these conditions fulfilled, the relation indicated by the following equation must hold:

$$[(Ag^+) - x] \times [(ac^-) - x] = S.P.$$

To tell whether a precipitate will be formed we have, therefore, only to substitute values in this equation and find whether x exceeds the value of (Ag ac) for a saturated solution.

Having made the calculation, test the validity of your conclusion by actually mixing the two solutions (20 cc. of each), and taking the proper precautions against supersaturation.

Procedure B.—Calculate whether the mixing of 20 cc. of N/5 sodium acetate with 10 cc. of N/5 silver nitrate should yield a precipitate of silver acetate. Note that when these solutions are mixed, the volume, so far as the sodium acetate is concerned, becomes 3/2 as great, making the concentration 2/3 the original concentration. For the silver nitrate

the volume becomes three times as great, giving the concentration 1/3 its original value. The degree of ionization may be obtained from the table by interpolation. Having done this, calculate the concentration of the two ions, and then proceed as in A to determine whether a precipitate should be formed. Finally test the calculation by actual experiment.

Procedure C.—If a precipitate is produced in B, the mixture thus obtained may be used here. Before going on, however, let the mixture stand for ten minutes with frequent stirring to make sure that no supersaturation exists. Proceed then as follows: Decant most of the liquid through a filter, leaving the remainder with the precipitate.

To the portion containing the precipitate, add three drops of concentrated nitric acid, and stir. Explain the result.

The filtrate is a saturated solution of silver acetate. What effect should it have to add a little solid sodium acetate? Carry out the experiment, adding 1 gm. of the salt (do not weigh), and stirring until dissolved. Explain the result.

Exp. 47. Precipitation by Means of Hydrogen Sulphide and its Salts.

Procedure A.—Take 30 cc. of $M/10$ zinc sulphate solution in a small Erlenmeyer flask and pass H_2S gas through it rapidly for five minutes. (This should be done in a hood where you are sure there is a good draft.) Filter off the precipitate of zinc sulphide and pass H_2S through the filtrate for five minutes. Repeat the process until nothing more can be precipitated in this way.

Test the clear filtrate with litmus, and explain the presence of the hydrogen ion, writing the proper equilibria.

Now divide the filtrate into two parts. To one part add an excess of ammonium hydroxide, and to the other part add solid sodium acetate. Was the zinc all precipitated by the H_2S? Does the presence of the hydrogen ion noted above have anything to do with this? Explain very carefully, writing the proper equilibria. The precipitate formed when ammonium hydroxide was added was zinc sulphide, not hydroxide. Explain its formation. Why was the same thing formed when sodium acetate was added?

Take another 30 cc. of the zinc sulphate solution, add an equal volume of normal HCl, and pass H_2S through it for five minutes. Explain the result. Why is zinc not precipitated by H_2S along with the members of the Copper Group in qualitative analysis?

Procedure B.—Take 30 cc. of $M/10$ cupric sulphate solution, add an equal volume of normal HCl, and pass H_2S through it rapidly for five minutes. Filter off the precipitate of cupric sulphide, and pass H_2S

through the filtrate for five minutes. Repeat the process until satisfied that nothing more can be precipitated in this way.

Now test the filtrate as follows to see whether the copper has been completely removed: Boil for about five minutes to remove the H_2S, and then cool by rotating the flask under a stream of cold water. Now divide into two parts. To one part add a bright piece of sheet zinc and let stand for a time. The zinc will show a red coating of metallic copper when the concentration is as low as 0.000008 gm. per cubic centimeter. Is there any evidence of its presence in this case? To the other portion add solid sodium acetate (about 1 gm.). This will nearly neutralize the free acid present. (Why?) Now add potassium ferrocyanide solution (1 cc.). If copper is present a cherry-red color will appear. This test will show the presence of 0.00001 gm. of copper per cubic centimeter.

Why is copper precipitated completely, even in the presence of hydrochloric acid, while zinc was not, even when starting with a neutral solution?

Procedure C.—Take 30 cc. of $M/10$ ferrous ammonium sulphate solution (freshly prepared), and pass H_2S through it. Is FeS (black) precipitated? Add ammonia to the solution, or add ammonium sulphide to a fresh portion. Explain the result.

Exp. 48. Precipitation of Magnesium by Means of Ammonium Hydroxide.

Procedure A.—Magnesium hydroxide is soluble in water to the extent of 0.009 gm. per liter at 18° C. Calculate this into terms of moles per liter (molar solubility). Assuming that the base is completely ionized at this great dilution, calculate first the concentrations of the ions Mg^{++} and OH^-, and from these calculate the solubility product $(Mg^{++}) \times (OH^-)^2$.

Suppose we were to mix molar ammonium hydroxide with an equal volume of $M/5$ magnesium sulphate, the former becoming thereby $M/2$ and the latter $M/10$, would a precipitate of $Mg(OH)_2$ be formed? $M/2$ NH_4OH is 0.57 per cent (0.0057) ionized. $M/10$ $MgSO_4$ is 37 per cent (0.37) ionized. Calculate the concentrations of the two ions Mg^{++} and OH^- resulting from this ionization, and then calculate the ion product $(Mg^{++}) \times (OH^-)^2$. Comparing this ion product with the solubility product calculated above, and making *no* allowance for the negligible amount of non-ionized Mg $(OH)_2$, decide whether a precipitate should be formed. Finally mix 20 cc. of each of the original solutions and note the result.

Is the magnesium all precipitated by the above process, or is there

still a considerable concentration of Mg^{++} ion in the solution? To determine this filter the solution and to the clear filtrate add 5 cc. of $M/10$ sodium phosphate. In the presence of magnesium ion a crystalline precipitate of $MgNH_4PO_4$ will result. Was much magnesium ion still present? Making use of the following equilibria,

$$MgSO_4 \rightleftarrows Mg^{++} + SO_4$$

$$NH_4OH \leftrightarrows OH^- + NH_4^+$$
$$\Updownarrow$$
$$Mg(OH)_2 \text{ (non-ionized)}$$
$$\Updownarrow$$
$$Mg(OH)_2 \text{ (solid)}$$
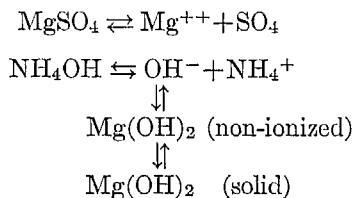
note what ions accumulate as $Mg(OH)_2$ is precipitated by NH_4OH, and what effect this accumulation has on the concentrations (Mg^{++}) and (OH^-). Which one will be affected the more, relatively? Explain now why the precipitation stopped when much magnesium was still present.

Procedure B.—Suppose we were to mix 20 cc. each of molar NH_4OH and $M/5$ $MgSO_4$, having previously added to one solution enough solid ammonium chloride to make the solution, *after mixing,* molar with respect to this salt. Would a precipitate of $Mg(OH)_2$ be formed? (The solutions after mixing total 40 cc., which equals 0.04 liter. We shall, therefore, need 0.04 mole of NH_4Cl.)

Molar NH_4Cl is 74 per cent ionized. Calculate the total NH_4^+ concentration; and then, applying the principle of the common ion effect, calculate the concentration of OH^- which must stand in equilibrium with this. From this and the known concentration of Mg^{++} calculate the ion product $(Mg^{++}) \times (OH^-)^2$. You are then able to decide whether precipitation of $Mg(OH)_2$ will occur. Having made the calculations perform the actual experiment.

Exp. 49. The Silver-Ammonium Complex.

Procedure A.—Place 10 cc. of $N/5$ silver nitrate in a small beaker and titrate rapidly with $N/5$ ammonium hydroxide until the precipitate first formed is redissolved, leaving nothing more than the faintest opalescence. Note the number of cubic centimeters of ammonia solution required to do this.

Judging from the titration values, should the complex take the form $AgNH_3$, $Ag(NH_3)_2$, or what? Is the complex an anion, or a cation? Write the formula of the salt of the complex formed in the above reaction. Also write an equation indicating the complete reaction between the silver nitrate and the ammonium hydroxide. What is the precipitate formed at first?

Procedure B.—Calculate whether a precipitate of silver chloride should be formed if we were to add 1 cc. N/10 sodium chloride solution to 10 cc. of the silver-ammonium nitrate solution, proceeding as follows:

The dissociation constant for the complex has the value indicated thus:

$$\frac{(Ag^+) \times (NH_3)^2}{(Ag(NH_3)_2{}^+)} = 7 \times 10^{-8}$$

The original concentration of the silver salt was 0.2. If the final volume of the solution after titration is three times as great as the original volume and each complex molecule contains one silver atom the concentration of the complex salt is 1/3 of 0.2, or 0.0666. Like any other salt, this complex salt is at this dilution about 90 per cent ionized. Calculate from this the concentration of the complex ion $Ag(NH_3)_2{}^+$.

The small size of the constant shows that the complex is only slightly dissociated. Therefore we may assume that the concentration of the undissociated part is practically the same as the total concentration of the complex. On the assumption that this is true, substitute its value in the equation and calculate the concentration of the silver ion Ag^+. [Let $x = (Ag^+)$, then $(NH_3) = 2x$, and we have for the numerator of the fraction $x(2x)^2$.]

When 1 cc. of N/10 NaCl is added to 10 cc. of the nitrate solution, its concentration becomes N/110, while that of the complex is scarcely changed at all. Calculate the Cl$^-$ concentration in N/110 NaCl, assuming 95 per cent ionization.

You now have the concentration of the silver ion and the chloride ion as they will be at the moment when you mix 1 cc. 0.1 N NaCl with 10 cc. 0.0666 N silver-ammonium nitrate. The solubility product for AgCl is 2×10^{-10} at 25° C. Find whether with the above concentrations of Ag^+ and Cl$^-$, a precipitate of AgCl should be produced.

Having made the calculation, verify by actual experiment.

Procedure C.—Will the complex give a precipitate of AgCl if we first add an equal volume of N NH₄OH and then add N/10 NaCl in the same proportions as in B?

Note that the concentration of both the complex and the NH₄OH are reduced to half their original concentrations by mutual dilution. In the case of the latter we are concerned in knowing the concentration of the NH₃. The total concentration (NH₃+NH₄OH) becomes 0.5 after mixing, and the concentration of the NH₃ may be taken as twice that of NH₄OH. From this $(NH_3) = 2/3$ of 0.5, or 0.33.

Letting x again stand for (Ag^+), we have for the numerator of the

fraction $x(0.33)^2$. Making the proper substitution for the denominator the value of x may be calculated at once.

Having thus determined the concentration of the Ag^+ ion, again apply the solubility product principle and determine whether a precipitate should be obtained.

Verify by actual experiment, starting with 10 cc. of the silver-ammonium nitrate solution, adding first an equal volume of N NH_4OH and then 2 cc. of N/10 NaCl.

Calculate also whether 6 cc. of N/10 NaCl should give a precipitate of AgCl, counting the Cl^- ion concentration three times that produced by the addition of 2 cc. Prove this also by experiment; that is, add 4 cc. more to the solution just tested.

Procedure D.—Would a precipitate of silver bromide be produced if KBr were substituted for NaCl in (C)?

The concentration of the Br^- ion may be taken as equal to that of the Cl^- ion as calculated in (C). The solubility product for AgBr is 4.4×10^{-13}.

When you have decided whether a precipitate should be produced, verify by adding 1 cc. N/10 KBr solution to 10 cc. of the mixture of 1 vol. silver-ammonium nitrate and 1 vol. normal NH_4OH.

Exp. 50.—The Ferric-oxalate Complex.

When ferric sulphate and ammonium oxalate are brought together the complex ammonium ferric-oxalate is formed according to the equation.

$$Fe_2(SO_4)_3 + 6(NH_4)_2C_2O_4 \cdot 2H_2O \rightarrow 2(NH_4)_3Fe(C_2O_4)_3$$
$$+ 3(NH_4)_2SO_4 + 12H_2O$$
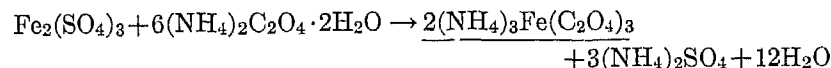
It will be noted that the weights of the reacting substances are nearly in the proportion of 1 : 2. To prepare the complex, therefore, weigh out 2 gm. ferric sulphate and 4 gm. ammonium oxalate, grind together in a mortar, and dissolve in 100 cc. of water without heating. Make the following tests with this solution:

(A).—To 10 cc. add 5 cc. 10 per cent solution of ammonium thiocyanate. Do you obtain a test for ferric ion?

Test another portion with ammonium hydroxide. What is the precipitate produced? Was ferric ion present? Point out the reason why these two tests give different results.

To another 10 cc. add 3 cc. 6 N HCl and then 5 cc. thiocyanate solution. Explain the result.

(B).—Test a small portion of the solution for oxalate ion by adding a solution of calcium chloride. Is oxalate ion present?

In another 10-cc. portion dissolve a piece of solid ferric chloride the size of a pea, and then test for oxalate ion as before. Explain.

Exp. 51. Amphoteric Nature of the Aluminum Group.

Procedure A. Aluminum.—To 5 cc. aluminum sulphate solution add a dilute solution of NaOH, drop by drop, with stirring, until a piece of red litmus paper placed in the solution barely shows a permanent blue color. The precipitate is aluminum hydroxide $Al(OH)_3$.

To show the amphoteric nature of this hydroxide, treat one portion of the above mixture with an excess of dilute NaOH and another with an excess of dilute HCl. Write equilibria to show the amphoteric ionization of $Al(OH)_3$, and then show how the equilibria are disturbed by adding NaOH and HCl respectively. Name the two ions containing aluminum.

To the above acid solution add an excess of dilute NH_4OH. What is the precipitate? Show how the equilibria are disturbed, and extend to include the solid phase (the precipitate). To the corresponding alkaline solution add a solution of ammonium chloride. Show how the equilibria are disturbed in this case.

Procedure B. Chromium.—To 5 cc. chromium sulphate solution add NaOH as in Procedure A, taking care not to use an excess. Treat separate portions of the mixture thus produced with NaOH and HCl as in A. Write equilibria here also, and show how they are disturbed by acid and alkali. Name the ions of chromium here involved.

Precipitate $Cr(OH)_3$ as above, place in a small casserole, add about 1 gm. of sodium peroxide, Na_2O_2, and heat to boiling until the green color gives place to a clear yellow. What does the yellow solution contain? What sort of reaction was this by which chromium ion, Cr^{+++}, was changed to chromate ion, CrO_4^{--}? Would aluminum ion act in the same way? Does chromium in this hexavalent form ever exhibit any basic properties; in other words, is hexavalent chromium amphoteric? Write the formula of a hypothetical hydroxide of hexavalent chromium. How is this related to chromic acid, H_2CrO_4? (Note also the change of $Al(OH)_3$ to $HAlO_2$.) How can hexavalent chromium be changed back to the trivalent form?

Procedure C. Iron.—Precipitate ferric hydroxide from a solution of the nitrate or chloride, proceeding as in A. Treat separate portions of the mixture with NaOH and HCl respectively. Is ferric hydroxide amphoteric? Write equilibria showing its method of ionization and the effect of H^+ ion, not forgetting the heterogeneous equilibrium involved.

Ferric hydroxide cannot be oxidized by the method used for chro-

mium.   To show, however, that iron does possess latent acidic prop-
erties, proceed as follows: Take 1 gm. of ferric oxide, mix with 4 gm. of
sodium peroxide in a small nickel crucible, and heat, gently at first,
finally to faint redness.   Cool the melt completely and dissolve out of
the crucible by placing in 50 cc. of ice-water contained in a small casse-
role.

The purple color of the solution is due to the presence of sodium
ferrate, Na_2FeO_4.   The iron is evidently hexavalent, and the salt is
related to, the hypothetical hydroxide, $Fe(OH)_6$, just as Na_2CrO_4 is
related to hypothetical $Cr(OH)_6$.   (Point out this relationship.)   Write
equilibria showing the acidic and possible basic ionization of $Fe(OH)_6$,
or better the anhydride form, $FeO_2(OH)_2$.   Which mode of ionization is
more pronounced?

The decomposition of the excess of Na_2O_2 makes the solution very
basic.   Could basic ionization of the above hydroxide occur in such
a solution?   Could basic ionization occur in an acid solution?   Sodium
ferrate is very unstable at best, but it has its greatest stability in a
strongly basic solution.   Dilute a portion of the concentrated solution
with 10 volumes of water and let stand for some minutes.   Acidify
another small portion, and note the extreme rapidity with which the
basic ion is reduced.   The difference in the rapidity of reduction in acid
and alkaline solution is very good evidence that the two modes of
ionization actually exist.

The most stable ferrate is probably that of barium, and the stability
in this case is probably due mainly to insolubility and consequent lack
of ionization.   It would be interesting to prepare this salt.   To do so,
carefully pour off the purple solution from the ferric oxide beneath it,
and to this solution add barium chloride solution as long as a precipitate
is produced.   Let the precipitate of $BaFeO_4$ settle, and decant the liquid.
Add water and filter on a Büchner funnel, washing the precipitate
thoroughly.   Dry, and then scrape from the paper and preserve as a
preparation.

Exp. 52. Amphoteric Nature of the Halogens.

Procedure A.   Displacement of Negative Iodine by the More Nega-
tive Bromine.—To 5 cc. of potassium iodide solution add 5 cc. of bromine
water.   Iodine is displaced.   Write the ionic equation showing this.

Procedure B.   Displacement of Positive Bromine by the More
Positive Iodine.—Weigh out on the laboratory balance 0.8 gm. of
potassium bromate, $KBrO_3$, and 0.6 gm. of solid iodine.   Grind the two
solids together in a mortar, transfer to a small flask, and add 10 cc. of
water.   Heat gently (not to boiling) in a hood with good draft.   Is

bromine displaced? Write an equation indicating the change. The product is potassium iodate.

Bromine in $KBrO_3$ or $HBrO_3$ is pentavalent positive. Write the formula of a hydroxide of this bromine. How is $HBrO_3$ related to this? Write equilibria showing both basic and acidic ionization of the penta-hydroxide or its anhydride form. If the basic ionization were encouraged, the pentavalent ion Br^{+++++} would be produced. What effect would this have on the speed of displacement by iodine? Weigh out a sample of $KBrO_3$ and iodine as above, grind together, and divide into two nearly equal portions. Place these in separate flasks, and add to each 5 cc. of water. To one then add 1 cc. of 6 N sulphuric acid. Let the two stand side by side for a time without heating, having them properly labeled to prevent confusion. Which one shows the greater speed of reaction? Explain fully.

CHAPTER XV

. ELECTROCHEMISTRY

Exp. 53. Determination of the Faraday.

Apparatus.—Copper coulometer, milliammeter, 150-ohm rheostat.
The plates of the coulometer are of copper,
24 gauge, each having a surface of about
25 sq. cm., counting both sides. Before
being used the first time they should be
rubbed bright with emery paper and washed
with alcohol to remove grease. After this
the surfaces which go below the solution
should not be touched. The arrangement
of the cell is seen in Fig. 24. The arms of
the plates have forked ends which enable
them to be easily attached or removed.
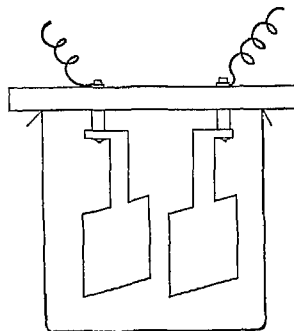
FIG. 24.

Procedure.—The solution used in the
coulometer is made up according to the following formula:

Pure $CuSO_4 \cdot 5H_2O$...	75 gm.
H_2SO_4.	25 "
Alcohol........	25 "
Water.....	500 "

It is best to first dissolve the copper sulphate by grinding with a
little water and gradually adding more until it is all in solution, and
then to add the acid and alcohol. The solution should be filtered unless
perfectly clear. After each experiment the solution should be returned
to the stock bottle. It may be used over and over indefinitely.

The determination is conducted as follows: Fill the cell about half full
of the copper solution, or so full that the wide part of the electrodes is
covered, and connect in series with a rheostat (150 ohms in), an ammeter,
and two storage cells (4 volts). Be sure that you know which way the
current is running, and leave one connection open until the apparatus
is inspected by the instructor (note 1). When everything is ready close
the circuit, and then adjust the rheostat so as to give a current of about
0.25 ampere (note 2). _Now, leaving all the connections and adjust-

ments undisturbed, remove the cathode and wash it, first with water and then with alcohol. Dry by pressing between two filter papers and then warming gently by holding high over a small flame. Finally cool and weigh accurately.

Now return the cathode to its place, and just at the moment when it is plunged into the solution take the time to a fraction of a minute. (It will be best to start exactly on the minute.) The ammeter reading should be the same as before, but it should be retaken and adjusted if necessary, and the value then recorded.

After about twenty-five minutes (note the exact time) break the connection, and then quickly wash and dry the cathode as before (note 3). Finally weigh the cathode and determine the weight of the copper deposited.

Calculate the number of seconds during which the current was running; and then, remembering that amperes multiplied by seconds give coulombs, calculate the number of coulombs of electricity used. This was the quantity of electricity required to deposit the copper you obtained. Calculate first the copper equivalent of the coulomb, and then the number of coulombs required to deposit one equivalent weight of copper. The latter is the faraday. The standard value for the former is 0.000329.

NOTES.—(1) The ammeter may be ruined by careless work. By having a high resistance in the instrument when first turning on the current, you will prevent trouble.

(2) If too heavy a current is used the copper ions will not be able to carry it alone, and some hydrogen will be deposited, that is, too little copper will be obtained. If too small a current is used some of the copper ions will only partially discharge, giving cuprous ions Cu^+. This again gives too little copper.

(3) Copper is slowly soluble in a solution of cupric ion, forming cuprous ion; hence the washing should be accomplished as quickly as possible.

Exp. 54. Electrode Reactions.

Apparatus.—A 6-in. U-tube with two platinum electrodes and one copper electrode (Fig. 25). This apparatus will be used for all the following experiments.

Procedure A. Electrolysis of Hydrochloric Acid with Platinum Electrodes.—Fill the U-tube with normal HCl until the electrodes are just covered.

FIG. 25.

Electrolyze, using 8 volts. After about five minutes raise the cathode and instantly apply a lighted match to the mouth of the

tube. Explain. Cautiously waft a little of the anode gas to the nostrils. What is it?

Show that one of the electrode reactions is reduction and the other oxidation.

Do not allow this electrolysis to proceed long. The reason is obvious.

Procedure B. Electrolysis of Hydrochloric Acid with Copper Anode and Platinum Cathode.—Make the proper change in the electrodes, and then proceed as in A. Is chlorine gas evolved? After ten minutes remove a little of the anode liquid and add to it an excess of ammonium hydroxide. What ion was present? Show exactly how it came there. (Do not dodge the question by saying that " copper was dissolved off the anode.")

Procedure C. Electrolysis of Sulphuric Acid with Platinum Electrodes.—Arrange the U-tube and electrodes as in A and electrolyze normal sulphuric acid, using 12 volts. Test the electrode products (gases). What are they? Explain their source. How would the results differ if a copper anode were used?

Procedure D. Electrolysis of Sodium Sulphate with Platinum Electrodes.—Electrolyze a normal solution of sodium sulphate, using 10 volts. What gases are evolved? Explain carefully their source. Test the cathode liquid with red litmus paper and the anode liquid with blue. Explain.

Procedure E. Pole Indicator.—Moisten a piece of red litmus paper with a solution of sodium chloride and place upon it, 1 cm. apart, the " lead " wires from a storage cell. At one pole the paper turns blue, at the other it is bleached white. Which pole is positive and which is negative? Explain.

Procedure F. Electrolysis of Ferric and Ferrous Salts.—Electrolyze a solution of ferric chloride, using platinum electrodes. After five minutes, test the cathode liquid for Fe^{++} by means of ferricyanide solution. Explain. Some metallic iron may be deposited. Explain. Test for it by immersing the cathode in warm 6 N HCl. Evolution of hydrogen indicates a metal, which must be iron.

Fill the U-tube with a solution of ferrous sulphate, and electrolyze as above. After five minutes test for ferric iron. (Where?) Use ammonium thiocyanate. What happens in this case at the other electrode?

Exp. 55. Migration Velocity of Hydrogen and Hydroxyl Ions.

Apparatus.—Same as in Exp. 52.

Procedure.—Prepare a 2 per cent stock solution of agar-agar as follows: Take 5 gm. of the powdered material, grind to a smooth, thin

paste with a small amount of water, then stir into it 250 cc. of boiling water, and boil for about two minutes.

Take 60 cc. of the agar solution (still hot), add to it 15 cc. of a saturated solution of potassium nitrate, 10 drops of phenolphthalein indicator, and 10 drops of N/2 NaOH. Mix thoroughly by pouring back and forth between two beakers several times. Now divide into two equal parts, and to one part add N/2 NHO₃ from a burette (about 4 drops), until the color of the indicator is just discharged after thorough stirring, and then add exactly the same amount in excess.

You now have two solutions, both of which will become solid jellies on cooling, both of which contain the same electrolyte (KNO₃), both containing the same indicator, one containing a small definite excess of H⁺ ion, and the other the same excess of OH⁻ ion.

Pour into the U-tube just enough of the alkaline solution to form a seal at the bottom; incline the tube so that one end of the solution comes near the center, and then cause the jelly to set by running cold water over the tube. When the jelly is solid enough to stand up well, fill the shorter arm of the tube with the alkaline, and the longer with the acid, solution, stopping in each case about 2 in. from the top of the tube. Now clamp the U-tube upon the ring stand and let the jelly set solid. Finally fill the end next the acid jelly with N/2 NaOH and that next the alkaline with N/2 HNO₃, insert the electrodes, and immediately turn on the current (16 volts), making the electrode in the NaOH the cathode. Take the time and allow the action to proceed for one hour.

You notice that the OH⁻ ion from the NaOH moves slowly towards the anode, coloring the indicator pink, while the H⁺ ion from the HNO₃ travels towards the cathode, removing the color of the indicator.

After one hour, measure the distances passed over by each of the two ions. If the tube had been left for one hour without turning on the current, the acid would have diffused over a distance of 1.5 cm. and the alkali 1.1 cm. (This has been determined by experiment.) In calculating the distances passed over in one hour through the influence of the applied potential, we must, therefore, subtract these amounts from the observed distances. Having done this, measure the average distance between the electrodes around the bend of the U-tube, and then calculate the potential gradient used. Calculate also what would have been the distances covered by the ions if the potential gradient had been 1. The standard values at 18° C. are H⁺ 11.52 cm. per hour, and OH⁻ 6.48 cm. per hour. Your values will be somewhat lower than these, because of the retarding influence of the jelly.

Exp. 56. Migration of a Complex Ion.

Apparatus.—The specially constructed U-tube which is seen in Fig. 26, and which permits one liquid to be run under another without mixing. When in use the apparatus is supported by a ring stand, the clamp grasping one of the arms of the U, *not the small tube at the back.* The corks supporting the electrodes are grooved to allow the escape of gases.

Procedure.—Prepare 25 cc. of a solution of cupric bromide containing 1 gm. $CuBr_2$ to 2.5 gm. water. Having the apparatus properly supported and the electrodes in place, fill the thistle tube with the solution, taking care that the air is all out of the connecting tube above the stop-cock; then cautiously let the solution flow around until it just reaches the bottom of the U. Now place in the U-tube enough normal nitric acid to stand about 1 inch high in the arms, and then cautiously let the copper solution in under the acid until the acid at the top just covers the electrodes.
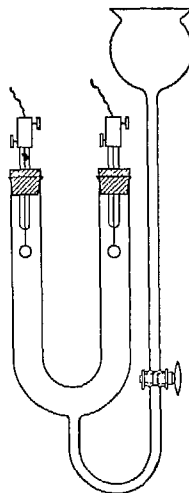
FIG. 26.

By means of a narrow gummed label, mark the boundary line of the brown solution on the side which is to be the cathode compartment, and then turn on the current (10 volts). Allow the action to proceed for half an hour.

In what direction does the copper ion move? Explain. In what direction does the boundary line of the brown move? If the brown color were due to undissociated $CuBr_2$ would it move at all? Why? To what may the brown color be due?

Exp. 57. The Daniell Cell.

Apparatus.—A glass tumbler of table size. A porous battery cup 4×8 cm. A 3-hole rubber stopper No. 7. A piece of 24-gauge sheet copper cut as seen in Fig. 27. Two zinc rods 10 cm.×6 mm. Voltmeter and ammeter of low range. Copper wire and connectors.
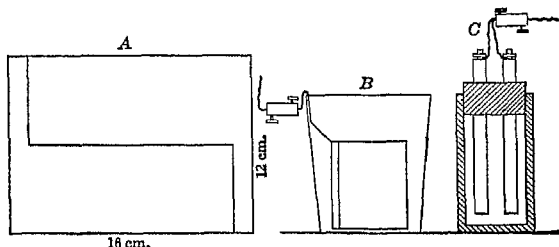
FIG. 27.

If the copper is taken in sheets of the size and shape shown in A, two electrodes can be made from one piece without any waste of material. The copper, after being cut, is rolled into a cylinder to fit the tumbler, and the arm is bent as seen in B to hold the electrode firmly upright. The zinc rods are inserted in the stopper as seen in C, and are connected to the copper " lead " wire.

Procedure A. E.M.F.—Having assembled the pieces of apparatus seen above, fill the porous cup about three-fourths full of normal zinc sulphate solution and insert the stopper carrying the zinc electrodes. Place the copper electrode in the tumbler, set the porous cup inside it, and then add, in the outer compartment, sufficient saturated solution of copper sulphate to cover the electrode.

You are first to measure the E.M.F. of the cell; but before doing this decide from which electrode the current will come, and if your voltmeter has more than one range, decide which range to use. Connect the electrode from which the positive current comes (the cathode) to the side of the voltmeter marked $+$, and the other to the binding post giving the proper range. Always be very careful not to connect any electrical measuring instrument backwards, or to use it with a current which is beyond its range.

When you are *sure* about these two points, connect the voltmeter and read and record the voltage of the cell. How does this voltage compare with the calculated value for the couple, $Zn/N \cdot Zn^{++} - N \cdot Cu^{++}/Cu$? Should it be just the same? Why?

Procedure B. Internal Resistance.—Connect the cell with an ammeter, taking the precautions noted above, and carefully take the reading. According to Ohm's law, $C = E/R$, or $R = E/C$. The copper wires and the ammeter offer practically no resistance, so the resistance R of the circuit is practically all inside the cell. Substitute for E the value found in A, and for C the present reading of the ammeter, and calculate R. Upon what does the internal resistance depend?

Procedure C. Effect of Concentration.—Remove the solutions from the cell, saving only the copper solution, and substitute for them the following: For the dilute zinc sulphate solution substitute a very concentrated solution of zinc chloride (note 1), and for the concentrated copper sulphate substitute one of $N/100$ concentration.

Now assemble the apparatus, as before, and take the voltage. Explain the change.

Add enough ammonium hydroxide to the copper solution to throw the copper into the blue complex, $Cu(NH_3)_4^{++}$. Note the effect on the voltage. Explain.

Finally add somewhat more than enough potassium cyanide solution

to remove the blue color of the copper-ammonia complex. The copper is now still more completely locked up than before by being thrown into the extremely stable complex, $Cu(CN)_2{}^-$. (*Caution: Potassium cyanide is dangerous; keep it off your hands, and also off the desk.*) Note the effect on the voltage, reversing the connections if necessary. Explain.

When through with the experiment, return the zinc chloride solution to the bottle and carefully wash out the apparatus. Pour the cyanide solution into the sink and immediately wash it down with water. Leave the apparatus filled with water.

NOTE.—Zinc chloride is used simply because of its great solubility.

Exp. 58.—A Concentration Cell.

Apparatus.—Same as for the Daniell cell, excepting that a zinc electrode is substituted for the copper.

Procedure.—Place in the porous cup the concentrated zinc chloride solution used above, and in the outside compartment use a solution of any zinc salt of $N/100$ concentration. Decide which way the current will flow, then connect in the proper way and take the voltage. Explain the source of the E.M.F. and the direction of the current.

Leave the apparatus filled with water.

Exp. 59. Decomposition Voltage.
    A. Decomposition Voltage of Sulphuric Acid with Platinum Electrodes.

Apparatus.—The coulometer cell used for Faraday's law. A pair of platinum electrodes of the same size and shape as the copper. A voltmeter and ammeter, both of low range. A rheostat of range 2200 ohms, 0.5 ampere.

Procedure.—Set the platinum electrodes in place, taking great care not to bend them, and fill the cell to the proper depth with normal sulphuric acid (note 1). Connect with voltmeter, ammeter, rheostat (2200 ohms in), and six storage cells (12 volts).

Now slowly turn out the resistance until the voltmeter reads 0.6, and then read the ammeter. Increase the voltage to 0.8, and again read the ammeter. Continue in this way until a voltage of about 1.6 is reached, and then make the intervals smaller for a few readings. Note the voltage where a marked increase in the amperage begins. This is the decomposition voltage. Take a few readings after the change is noted, to complete the list, but do not let the amperage go above 0.5.

Plot the values obtained on coordinate paper, making voltages abscissæ and amperages ordinates, and then draw a *smooth* curve. The decomposition point can then be plainly seen.

NOTE.—Normal sulphuric acid does not give normal ion concentration, for it is only about 0.5 ionized; but this slight difference has no appreciable effect on the decomposition voltage.

B. Decomposition Voltage of Sulphuric Acid with Mercury Cathode.

Apparatus.—Same as in A, excepting that a copper connecting wire, which reaches from the binding post on the cell cover to the bottom of the cell, is substituted for one of the platinum electrodes. This makes the connection with the mercury cathode. It is rubber-insulated where it passes through the liquid.
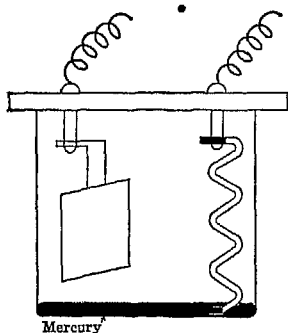
Mercury

FIG. 28.

Procedure.—Place in the cell a layer of clean mercury just sufficient to cover the bottom, and upon this place the normal sulphuric acid as above. When the cover is in place, the foot should be entirely covered with mercury—no uninsulated copper should come into contact with the acid. Proceed to determine the decomposition potential exactly as in A, plotting the values on co-ordinate paper.

Discuss the subject of overvoltage, and show its relation to the results of this experiment (for table of hydrogen potentials on various metals, see below):

POTENTIAL OF HYDROGEN ON VARIOUS METALS
(Sign of Solution)

H_2 on Hg	+0 51
H_2 on Zn.....	+0 43
H_2 on Pb.	+0 37
H_2 on Sn..	+0 26
H_2 on Cu	−0 04
H_2 on Ni.	−0 06
H_2 on Ag.......	−0.12
H_2 on Pt (smooth)	−0.18
H_2 on Fe.	−0.19
H_2 on Pt (black).	−0.27

Exp. 60. Displacement Reactions.

Procedure A. Action of Iron and Zinc on the Ions of Tin.—Take 20 cc. of stannic chloride solution, add to it 2 cc. of concentrated hydrochloric acid, and divide between two test-tubes. In one put a piece of sheet zinc, and in the other a piece of iron wire which has been previously cleaned with emery paper and rolled into a neat helix. Warm

both tubes to start the reaction, and then set aside for fifteen minutes. The action will be somewhat slow, because a solution of stannic chloride does not contain much stannic ion.   During the act of solution most of the tin will have gone into the form of the complex anion $SnO_3^=$.   (Explain the effect of HCl on t is.)

After fifteen minutes note what has occurred.   Has metallic tin (gray, leathery flakes) appeared in both cases?   Explain its presence or absence.   What has occurred in the solution containing the iron wire? Test for stannous ion by the common qualitative reaction.   Explain.

Take 5 cc. of stannous chloride solution and add a piece of sheet zinc. Can you account or the exceedingly rapid displacement of the tin?

Procedure B. Selective Displacement.—Take 3 cc. of stannous chloride solution, 3 cc. of antimony trichloride solution, and 2 cc. of 6 N HCl.   In this mixture place a coil of clean iron wire, heat if necessary to start the reaction, and then leave for fifteen minutes.   At the end of this time remove the wire, and carefully wash the precipitate by decantation until the wash water no longer gives a test for Sn^{++}.   What is the precipitate?   From your observation in (A) would you expect it to contain tin?   Treat the precipitate with 1 cc. of concentrated HCl. Is there any evidence that a metal is " dissolving," i.e., is hydrogen displaced?   After five minutes, dilute the acid solution with two volumes of water, filter, and test for tin.   Remove the black residue to a casserole and treat with 2 cc. 6 N HCl and 2 drops *only* of concentrated HNO_3, warming until solution is complete.   Dilute with 10 cc. of water, and add a solution of hydrogen sulphide.   An orange-colored precipitate of Sb_2S_5 indicates antimony.

Why is antimony displaced by iron while tin is not?   Why did antimony not dissolve when the precipitate was treated with concentrated HCl as above?   When antimony dissolves in aqua regia, as above, does it displace anything?   What does it do?

Procedure C. Hydrogen Displacement and Overvoltage.—In deciding whether a metal will " dissolve " in an acid, that is, displace hydrogen ion, it is not sufficient to note that hydrogen stands below this metal in the potential series.   In giving hydrogen its position in the potential series we were assuming that its potential was measured on the surface of a platinized platinum electrode.   On the surface of any other metal, its potential, and consequently its position in the series, might be widely different.   Consult the table above and note where hydrogen would be placed if its potential were taken on the surface of mercury; on silver; on lead.

Place 50 cc. of 3 N hydrochloric acid in a small beaker.   Into this dip a strip of clean sheet zinc.   Note that it immediately begins to

dissolve, displacing hydrogen ion.   Explain.   Is the potential of hydro-
gen on zinc above, or below, that of zinc itself?

Remove the zinc from the acid and bring it into contact with a small
drop of mercury.   Rub this over the surface until the coating of amal-
gam is perfectly homogeneous.   Now place the strip again in the acid.
Is hydrogen displaced?   Note that the amalgam on the surface is
really a solution of zinc in mercury, so that the zinc is still in contact
with the acid as it was before.   But the hydrogen must now come off
on a surface of mercury.   Is the potential of hydrogen on mercury
above, or below, that of the zinc itself?   (See table above.)   Does this
account for what you observe?

Now, if we offer another metal surface in contact with the amal-
gamated zinc, where the potential of the hydrogen will be lower than
that of zinc, we should expect the displacement of hydrogen by zinc to
proceed.   Referring to the table, would you consider iron, or lead, to be
the better for this purpose?   Test by taking clean strips of these metals
and holding them under the acid in contact with the amalgamated zinc.

APPENDIX I

General Outline of Laboratory Work

The following outline shows in some detail the author's time schedule covering the laboratory work for the whole second year course:

First Semester

Weeks.

1	Registration, preliminary laboratory work, including checking over apparatus, etc.
2, 3, 4	Experiments 1–11 inclusive. Groups as outlined under Appendix II below.
5, 6, 7, 8	Experiments 12–19 inclusive, all individual work
9, 10, 11, 12, 13, 14, 15	Gravimetric analysis. Constant application of principles, and practice in calculation.
16, 17	Experiments 20–25 inclusive. Groups on 24 and 25; 26 optional.
18	Examination week.
	Second Semester
1, 2, 3	Experiments 27–35 inclusive. Groups on 28, 31, 32, 33.
4, 5, 6, 7, 8, 9, 10	Volumetric analysis. Constant application of principles, and practice in calculation.
11, 12, 13, 14	Experiments 32–52 inclusive. Groups on 32, 33, and 41B; 43 optional.
15, 16	Experiments 53–59 inclusive. Groups as outlined under Appendix II below. Exp. 60. Checking out.
17, 18	Examinations and commencement.

It will be noted that more time seems to be assigned to the theoretical work than to the practical analytical work.   This is really not the case, for several of the theoretical experiments involve accurate analytical work.   The time is about evenly divided between the two types of work.

APPENDIX II

Grouping of Students for the Use of Special Apparatus

The laboratory work covering certain topics requires special apparatus, of which only a limited number of pieces will be available. In such cases the only feasible way to proceed is to assign the experiments in such a way that the smallest possible number of students will on any given day be working on the same experiment. There are two groups of experiments in the manual where this procedure is particularly necessary, namely Exps. 1–11 and Exps. 53–59. The procedure for the first group has been as follows: The first three experiments are short, and so may be finished in one period of three and a half hours. The other eight will occupy a period each, if properly done. This makes it possible to do the whole eleven in nine periods, or three weeks, where a student puts in three periods per week. To avoid confusion and induce students to study the experiments ahead, it is suggested that the instructor prepare a chart containing the students' names to whom the experiments are severally assigned so as to have the smallest possible number on any one experiment at a time, and so that each student will be doing the experiments in as nearly the normal order as possible. The following chart will make this clearer.

In the course for which the chart was prepared, the work began on Wednesday. The stars indicate the days elected by the student. Thus, student A elected Monday, Wednesday and Friday, student B, Monday, Thursday and Friday, etc. The experiments were assigned to A, B, C, D in the normal order. This brings A and C on 1, 2, 3, together and A, B, and C on 4 together. E, F, and G start off with 4, H and I with 5, etc. If only nine students are due on Wednesday, each can be given a separate experiment. If the number is eighteen two students will start working on each experiment, etc. Note that after a student once begins, the experiments follow on in normal order for him, although he may begin with number 5 or 6.

Experiments 53–59 can be arranged to cover four periods, thus: (53–54), (55–56), (57–58), (59). The charting is done exactly as indicated above, and so needs no comment.

Stu-dent	Wed	Thur.	Fri	Mon	Tue	Wed.	Thur	Fri	Mon	Tue.	Wed.	Thur.	Fri.	Mon	Tue.
A	123		4	5		6		7	8		9		10	11	
B		123	4	5			6	7	8			9	10	11	
C	123		4	5		6		7	8		9		10	11	
D			123	4	5			6	7	8			9	10	11
E		4	5		6		7	8		9		10	11		123
F	4		5	6		7		8	9		10		11	123	
G	4		5	6		7		8	9		10		11	123	
H	5		6	7		8		9	10		11		123	4	
I	5		6	7		8		9	10		11		123	4	
J		6	7	8			9	10	11			123	4	5	
K	6		7	8		9		10	11		123		4	5	
Etc.															

Where single experiments are encountered which call for special apparatus, the grouping can be arranged after the students come to the laboratory. Examples of this sort are experiments 24, 25, 28, 31, 32, 33, 41B. All that is necessary in these cases is to see that there are not too many working together. The group will sometimes tend to rush through the experiment and finish in the middle of the period. In such cases they should repeat, and in any case they should not be allowed to go faster than the schedule requires.

Attention may be called here to the general schedule outlined in the preface to the text, where the time required for large groups of experiments is indicated. No trouble will be experienced in actually getting the experiments done in the time specified, provided the time spent in laboratory work is as there indicated (nine or ten hours per week for thirty-two weeks).

APPENDIX III

Data and Suggestions Regarding Individual Experiments

As used by the author, the course of experiments given in this manual is made to occupy about half the time of a student working nine hours per week for thirty-two weeks. With that arrangement it is necessary to furnish much of the apparatus in a set-up form, and in some cases also to furnish standard solutions. The following notes indicate what is furnished in this way, and incidentally give some suggestions about the experiments themselves. A list of the materials and reagents which must be looked after is also given in each case Note that where a reagent has already been prepared, the fact is indicated by a cross reference, e.g., " as in 29." Sample values are given where possible, to indicate what may be expected in the way of accuracy.

Exp. 1. Brownian Movement.
   Apparatus.—Microscope and slides.
   Chemicals.—Gamboge.

Exp. 2.—Evaporation in Vacuum.
   Apparatus.—Two vacuum desiccators containing 5-cm. watch glasses. The air pump used is a Cenco-Nelson, run by a $\frac{1}{8}$ H.P. motor. The pump and motor are fastened on a wooden base, arrangement being made for taking up the slack of the belt. On the same base are also a closed tube manometer and a trap to prevent oil from being drawn back into the apparatus.
   Pressure tubing, tied in place with waxed cord, will be needed in making the connections.
   Results.—Time 1 hour 30 minutes. In second desiccator 0.8 gm. left.

Exp. 3. Boyle's Law.
   Apparatus.—The Boyle's-law apparatus. The mercury becomes dirty in time, probably on account of sulphur in the rubber stopper near it. This will adhere to the end of the tube containing the compressed air and allow an occasional bubble to creep in. This, of course, will slightly change the value of PV.

Students are very likely to read the barometer in millimeters and values on the apparatus in centimeters and then add the figures directly.

If students are careless about handling the tubes, the air may be warmed. PV will then grow larger as they proceed with the experiment.

Results.—PV = 1712, 1713, 1715, 1722. The gradual increase here probably indicates a slight rise of temperature.

Exp. 4. Partial Pressures and Volumes.

Apparatus.—All is furnished as seen in the sketch. The absorbing solution consists of 1 : 1 ammonia nearly saturated with NH_4Cl. The copper may be in the form of turnings or in fine strips of foil cut like " excelsior." The mixture thus prepared will absorb many liters of oxygen without apparent deterioration. A large, heavy ring stand, having a shelf attached to a ring, is needed to support the absorption tubes.

Results.—Volume N_2 76.3 cc.; O_2 19.9 cc.; Ar 0.8 cc.; H_2O 2.83 cc.

Exp. 5. Charles' Law.

Apparatus.—Furnished as shown. The tube containing the index is kept in a long thermometer box, always with the drying tube attached. Care should be taken not to shake it or the index may be separated into several parts.

Results.—If the bore of the tube is *uniform* and *no moisture* gets in, the results will be good. Sample value, 0.00363.

Exp. 6. Diffusion.

Apparatus.—Furnished as shown.

Exp. 7. Diffusion and Molecular Weights.

Apparatus.—Furnished as shown. If any of the gases are furnished in cylinders, reducing valves must be attached. If the clay cylinders are frail, they may be supported by tying a strong cord about the open end.

Results.—Time of outflow for O_2, 9.84 min.

Time of outflow for CO_2, 11.23 min.

$t/t = 0.87 \ \sqrt{32}/\sqrt{44} = 0.85.$

Time of outflow for H_2, 2.76 min.

Mol. wt. of $H_2 = 2.48$; calculated for H_2+water vapor, 2.42.

Exp. 8. Vapor Pressure of Water.

Apparatus.—Furnished as shown. Apparatus must also be provided for heating the U-tubes. Use a 3-qt. graniteware stock pot (13 cm. deep) insulated with asbestos paper and covered with a thick piece of asbestos board containing a slot for the U-tube.

Wool is used because wet cotton packs too closely.

Results.—A little low always, because of the imperfect drying power of calcium chloride. A sample value is 14.81 mm. instead of 15 mm.

Exp. 9. Heat of Evaporation.

Apparatus.—Furnish only the condenser with the three connecting tubes. The transite board is a part of each student's equipment.

The balance referred to is a " trip " with agate bearings. If properly cared for, these balances will weigh closer than 0.1 gm. It is a great advantage to have on the balance a 12-cm. evaporating dish with counterpoise. Students will need some encouragement to use this, however; they seem to like to spill chemicals about.

Ice is needed for this experiment and for several others in the course. It is a good thing to have an ice-box in the basement of the laboratory for this and other courses, particularly the organic, and to keep this filled all the time.

Results.—526 cal., 532 cal.

Exp. 10. Molecular Weight of Carbon Dioxide.

Apparatus.—A Kipp generator for CO_2. The tubes A and B are connected as seen, and attached permanently to a wooden base. The student prepares the rest of the apparatus. The air blast will be needed, as in 11.

Results.—43.8, 44.1.

Exp. 11. Molecular Weight of Ether.

Apparatus.—Furnish the Dumas bulb arranged as seen, also the bulb holder and the thistle tube. The rings of the bulb holder should be covered with rubber tubing, to prevent breaking the bulb. Attach permanently to the air-blast line a slender brass tube to dry out the bulb.

Chemicals.—The ether should be pure and " dried over sodium."

Results.—75.8, 75.0.

Exp. 12. Composition of Silver Oxide.

Apparatus.—Student's outfit.

Chemicals.—$AgNO_3$; stick NaOH, " pure by alcohol."

Results.—A little low, Ag = 93.01, 92.8, 93.03.

Exp. 13. Composition of Silver Chloride.

Apparatus.—Outfit.

Chemicals.—Prepare suspension of asbestos for Gooch crucibles. 6 N×HCl will also be needed.

Results.—Ag 75.36 per cent, Cl 24.64 per cent.
　　　　　Ag 75.26 per cent, Cl 24.74 per cent.

Exp. 14. Multiple Proportions.

Apparatus.—Outfit.

Chemicals.—Suspension of asbestos as in 13; $HgCl_2$; $HgCl$; stick NaOH, as in 12; $N/5$ $AgNO_3$ (34 gm. $AgNO_3$ per liter).

Results.—Cl per 1 gm. Hg; 0.1775 in $HgCl$, 0.3528 in $HgCl_2$.

Exp. 15. The Law of Volumes.

Apparatus.—The combustion tubes are loaned to the students for the day only. The students can fill them easily by attaching a large-bore funnel-tube to one end and then slowly shaking the oxide in.

The pneumatic pans are made of copper; they are 12×8 inches horizontally, and 7 in. deep. Keep them in the laboratory for common use.

Chemicals.—CuO, wire form; soda-lime; conc. ammonia; long-fiber asbestos.

Results.—N_2 167 cc., H_2 505 cc., NH_3 334 cc.

Exp. 16. Specific Heat and At. Wt. of Tin.

Apparatus.—Delicate thermometers, range 0–50° in 0.1°. About five will do for a class of 30. These may be kept in the storeroom, but better by the instructor. Small pocket lenses.

Chemicals.—Granulated tin, 30 mesh. Better sift out the particles as small as 60 mesh. Students will heat the tin with direct flame to dry it, and will surely melt it down.

Results.—0.0533, approximate atomic weight 120.

Exp. 17. Valence of Sodium, Magnesium, and Aluminum.

Apparatus.—Furnish only the capsules (No. 1).

Chemicals.—Sodium under benzene; magnesium, and aluminum wire No. 12, cut in 12-cm. lengths. It is a good thing to help the students when they are cutting sodium.

Results.—Cc. of H_2; Na 147, Mg 274, Al 438.

Exp. 18. Oxidizing and Reducing Valence.

Apparatus.—Outfit.

Chemicals.—Stock solution of $N/10$ iodine (12.7 gm. I_2 ground up with about 25 gm. KI, and dissolved in water to make 1 liter); $Na_2S_2O_3 \cdot 5H_2O$; starch; $KMnO_4$; $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$; $K_2Cr_2O_7$; conc. and 6N H_2SO_4; KI, 10 per cent solution.

Results.—
I_2, 25 cc. $= Na_2S_2O_3$, 25.1 cc.
$KMnO_4$, 10 cc. $= Na_2S_2O_3$, 50 cc.
$KMnO_4$, 9.8 cc. $= FeSO_4$, 50 cc.
$K_2Cr_2O_7$, 5 cc. $= Na_2S_2O_3$, 30 cc.

Exp. 19. Jones Reductor.

Apparatus.—The Jones reductor, fitted up as directed with zinc, etc. One is enough for a class of thirty.

Chemicals.—$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ and $KMnO_4$, as in 18.

Results.—50 cc. iron solution required 10 cc. $KMnO_4$ solution before passing through the reductor and 10.1 cc. after.

Exp. 20. Supersaturation of Sodium Sulphate.

Apparatus.—*Outfit.

Chemicals.—Na_2SO_4, anhydrous; cotton.

Exp. 21. Test for Potassium.

Apparatus.—Outfit.

Chemicals.—Tartaric acid; KNO_3.

Exp. 22. Normal Acids.

Apparatus.—Hydrometers, range 1–1.2, with tall cylinders ($4\frac{1}{2} \times 24$ cm. inside); 50-cc. graduated flasks. The flasks should be calibrated by filling with an *accurate* pipette and remarking.

Chemicals.—Stock solutions of approximately 6N acids (HCl, HNO_3, H_2SO_4). These are tested out *when cold* to see that their gravity really comes on the tables given.

Exp. 23. Normal Sodium Hydroxide.

Apparatus.—Outfit.

Chemicals.—NaOH, as in 12; methyl orange indicator (0.1 per cent solution in water).

Results.—NaOH checks with HCl; 25.7 cc. NaOH = 25.9 cc. HNO_3; 24.3 cc. NaOH = 24.6 cc. H_2SO_4.

Exp. 24. Freezing-point Lowering.

Apparatus.—The whole set-up as indicated: five sets for a class of thirty, allowing four to work together. (Note thermometer with range − 10 to +50.)

Chemicals.—Absolute ethyl alcohol; sal and ice for refrigeration.

Results.—Average of three readings, 1.85°.

Exp. 25. Molecular Weight of Propyl Alcohol.

Apparatus.—As in 24.

Chemicals.—Absolute propyl alcohol; salt and ice as in 24.

Results.—61.6, 61.25.

Exp. 26. Osmotic Pressure.

Apparatus.—Diffusion thimble, Schlericher and Schull, No. 579 (16×100 mm.); glass adapter; capillary tube; tall cylinder.

Chemicals.—Cane sugar. Color the sugar solution with a little methyl violet.

Exp. 27. Salt Effect.

Apparatus.—Outfit.

Chemicals.—Methyl orange indicator, as in 23; N $HC_2H_3O_2$ (57.1 cc. glacial acetic acid, sp. gr. 1.055, per liter); pure neutral NaCl; N NH_4OH (66 cc. conc. ammonia, sp. gr. 0.90, per liter); M/5 $MgSO_4$ (49 gm. $MgSO_4 \cdot 7H_2O$ per liter).

Exp. 28. Ionization of Sodium Chloride.

Apparatus.—As in 24.

Chemicals.—Pure NaCl, as in 27; salt and ice, as in 24.

Results.—78.3 per cent—high value due to hydration.

Exp. 29. Chemical Tests.

Apparatus.—Outfit.

Chemicals.—(A) M. H_3PO_4 (68 cc. conc. acid, sp. gr. 1.7, per liter). Sheet zinc in pieces 1×2 cm.; brass wire gauze, 40 mesh, pieces 2×4 cm.; N $HC_2H_3O_2$, as in 27.

(B) $FeCl_3$ sol., 5 per cent; NH_4SCN sol., 5 per cent; $K_3Fe(CN)_6$ sol., 5 per cent; $K_3Fe(C_2O_4)_3$ sol.—Prepare by grinding up about 5 gm. anhydrous $Fe_2(SO_4)_3$ with about 10 gm. $K_2C_2O_4$, and dissolving in 600 cc. water.

(C) NaCl sol., 5 per cent; $KClO_3$ sol., 5 per cent; $AgNO_3$, test sol.

(D) H_3BO_3 sol., 5 per cent; methyl orange, as in 23.

(E) $HgCl_2$ sol., 5 per cent; $Hg(NO_3)_2$ sol., 5 per cent; $K_2Cr_2O_7$ sol., 5 per cent.

Exp. 30. Hydrolysis of Methyl Acetate.

Apparatus.—Outfit.

Chemicals.—Methyl acetate. The commercial article usually contains methyl alcohol, acetone, and water. A fairly good grade can be made from this by shaking with a saturated solution of $CaCl_2$ and redistilling. The pure ester can be obtained commercially. M. H_3PO_4 as in 29; phenolphthalein, 1 per cent sol. in alcohol.

Results.—Cubic centimeters of N acetic acid produced:

With HCl	10.1
" HNO₃	9.62
" H₂SO₄	6.1
" H₃PO₄	2.7

Exp. 31. Heat of Neutralization.

Apparatus.—Thermometer, range 0–50° in 0.1°.

Results.—NaOH and HCl, 13893 cal; NaOH and HNO_3; 13831 cal.

Exp. 32. End Point of Methyl Orange.

Apparatus.—Comparator.—This is made of pine or cypress boards 5/16 in. thick, and is of the following dimensions: length 3 ft.; ends 1 ft. high by 8 in. wide; width of bars $3\frac{1}{2}$ in.; space between bars 4 in; seventeen holes $1\frac{3}{8}$ in. in diameter.

The Nessler's tubes are 31×220 mm.; 100-cc. mark 45 mm. from the top; bottoms cut flat.

Chemicals.—Methyl orange, as in 23.

Results.—2×10^{-4}, always.

Exp. 33. End Point of Phenolphthalein.

Apparatus.—Same as in 32.

Chemicals.—Phenolphthalein indicator, as in 30.

Results.—Rather poor.

Exp. 34. Choice of Indicator.

Apparatus.—Outfit.

Chemicals.—N acetic acid, as in 27; N NH_4OH, as in 27.

Exp. 35. Titration of Polybasic Acids.

Apparatus.—Outfit.

Chemicals.—M H_3PO_4, as in 29; $NaHCO_3$; Na_2CO_3 anhydrous; indicators as before.

Exp. 36. Speed of Reaction.

Apparatus.—Outfit.

Chemicals.—Methyl acetate, as in 30; phenolphthalein indicator, as in 30.

Results.—

Relative speed calc.	Relative speed obs.	K.
1	1	10.5
1.93	1 78	9.8
2	2.03	10.7
3.87	3.53	9.7

Exp. 37. Equilibrium Constant.

Apparatus.—Outfit.

Chemicals.—Methyl acetate, as in 30; glacial acetic acid; pure anhydrous methyl alcohol.

Results.—The two values for K were, in different cases:

> 7.3 and 8.4
> 6.9 and 7.3
> 8.7 and 8.4, the value depending on the temperature.

Exp. 38. Ionic Equilibrium.

Apparatus.—Outfit.

Chemicals.—$CuBr_2$; NaBr; $Cd(NO_3)_2$.

Exp. 39. Common Ion Effect.

Apparatus.—Outfit.

Chemicals.—M acetic acid, as in 27; $NaC_2H_3O_2 \cdot 3H_2O$; N/10 NH_4OH.—Students prepare from M (27); NH_4Cl; methyl orange and phenolphthalein.

Results.—Correspond exactly with calculated values.

Exp. 40. Neutralization Effect.

Apparatus.—Outfit.

Chemicals.—$NaC_2H_3O_2$, as in 39; methyl orange; congo red (1 per cent sol. in 30 per cent alcohol); NH_4Cl, as in 39; thymolphthalein indicator (1 per cent sol. in alcohol).

Results.—As calculated.

Exp. 41. Hydrolysis.

(A) Apparatus.—Outfit.

Chemicals.—Five per cent solutions of $NaC_2H_3O_2$, K_2CO_3, $AlCl_3$, NaCl, NH_4Cl; red and blue litmus solutions (extract 20 gm. of the powdered cubes twice with 200 cc. hot water. Let stand in tall beaker to settle and decant clear liquid through a Büchner. Make up to 600 cc. divide into two portions, and redden one portion with a drop or two of HCl).

(B) Apparatus.—Comparator and Nessler's tubes.

Chemicals.—Aniline sulphate; methyl orange.

Results.—Calculated value, 0.0151; observed, 0.0115.

Exp. 42. Dehydration of Copper Sulphate Pentahydrate.

Apparatus.—Outfit.

Chemicals.—$CuSO_4 \cdot 5H_2O$.

Results.—Loss at 200°, 3.97 mol. H_2O; at 250°, 4.96 mol. H_2O.

Exp. 43. Partition of Bromine.

Apparatus.—100-cc. glass-stoppered bottles; about 1 dozen pairs will be needed for a class of thirty. These are best kept by the instructor.

Chemicals.—Bromine water, conc.; 10 per cent sol. of KI, as in 18; $Na_2S_2O_3$, as in 18; CCl_4.

Results.—Values for K in the two cases, 25.1, 26.

Exp. 44. Partition of Succinic Acid.

Apparatus.—Same as in 43.

Chemicals.—M/10 succinic acid (about 12 gm. $(CH_2COOH)_2$ per liter); dry ether.

Results.—K in the two cases, 6.8 and 6.9.

Exp. 45. Phase Rule.

Apparatus.—Outfit, reading lens.

Chemicals.—$Na_2SO_4 \cdot 10H_2O$.

Results.—Very exact; the non-variant system continues for about two hours.

Exp. 46. Precipitation of Silver Acetate.

Apparatus.—Outfit.

Chemicals.—N/5 sodium acetate (27.2 gm $NaC_2H_3O_2 \cdot 3H_2O$ per liter); N/10 $AgNO_3$ (17 gm. $AgNO_3$ per liter); N/5 $AgNO_3$, as in 14.

Exp. 47. Precipitation of Sulphides.

Apparatus.—Outfit; an H_2S generator which the student may make for himself

Chemicals.—M/10 $ZnSO_4$ (29 gm. $ZnSO_4 \cdot 7H_2O$ per liter); FeS, granulated; NH_4OH; sodium acetate, as in 39; M/10 $CuSO_4$ (25 gm. $CuSO_4 \cdot 5H_2O$ per liter); sheet zinc, as in 29; sodium acetate as in 39; $K_4Fe(CN)_6$, 5 per cent; $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, as in 18.

Exp. 48. Precipitation of Magnesium.

Apparatus.—Outfit.

Chemicals.—M NH_4OH, as in 27; M/5 $MgSO_4$, as in 27; NH_4Cl; Na_2HPO_4, 5 per cent sol.

Exp. 49. Silver-ammonium Complex.

Apparatus.—Outfit.

Chemicals.—N/5 $AgNO_3$, as in 14; M/5 NH_4OH—student prepares from M NH_4OH (27); N/10 NaCl (approximately 5.8 gm. per liter); N. NH_4OH as in 27; N/10 KBr (approximately 12 gm. per liter).

Results.—As calculated.

Exp. 50. Ferric-oxalate Complex.

Apparatus.—Outfit.

Chemicals.—Anhydrous $Fe_2(SO_4)_3$; $(NH_4)_2 C_2O_4 \cdot 2H_2O$; NH_4SCN sol., as in 29; $CaCl_2$ sol., 5 per cent; $FeCl_3$, granulated.

Exp. 51. Amphoterism.

Apparatus.—Small nickel crucibles.

Chemicals.—5 per cent $Al_2(SO_4)_3$; dilute $NaOH$ and NH_4OH prepared by student; 5 per cent $Cr_2(SO_4)_3$; 5 per cent $FeCl_3$ sol. as in 29; Na_2O_2; Fe_2O_3; 5 per cent $BaCl_2$ sol.

Exp. 52. Amphoteric Bromine.

Apparatus.—Outfit.

Chemicals.—Sol. of KI, as in 18; bromine water, as in 43; $KBrO_3$; I_2.

Exp. 53. Faraday's Law.

Apparatus.—Coulometer with two copper electrodes; ammeter of low range; rheostat, 26 ohms; connecting wires.

Chemicals.—Special copper sulphate solution, see Exp.; alcohol, 96 per cent.

Exp. 54. Electrode Reactions.

Apparatus.—U-tube with two platinum electrodes and one copper electrode; wires.

Chemicals.—Na_2SO_4, 5 per cent; $FeSO_4$, 5 per cent; $FeCl_3$; $K_3Fe(CN)_6$, and NH_4SCN as in 29.

Exp. 55. Migration of Hydrogen and Hydroxyl Ions.

Apparatus.—Duplicate of 54.

Chemicals.—Agar-agar (powdered); sat. sol. of KNO_3.

Results.—Low, but relatively correct: H^+ 7.03 cm. OH^- 3.75 cm.

Exp. 56. Migration of Copper ions.

Apparatus.—Special U-tube with electrodes and wires.

Chemicals.—Sol. of $CuBr_2$ (1 gm. $CuBr_2$: $2\frac{1}{2}$ gm. water).

Exp. 57. Daniell Cell.

Apparatus.—Daniell cell with sheet-copper electrode; wires; voltmeter and ammeter of low range.

Chemicals.—N $ZnSO_4$ (144 gm. $ZnSO_4 \cdot 7H_2O$ per liter); saturated $CuSO_4$; conc. $ZnCl_2$; N $CuSO_4$ (125 gm. $CuSO_4 \cdot 5H_2O$ per liter); sol. of KCN, 5 per cent.

Students are very likely to get copper solution inside the porous cup. This deposits copper on the zinc rods and then brings about local action

and change of voltage.   The rods should be frequently cleaned (scraped or sandpapered).

   Results.—Close to calculated values.

Exp. 58. Concentration Cell.

   Apparatus.—Same as in 57, but with sheet-zinc electrode.

   Chemicals.—0.01 N $ZnSO_4$, prepared by student from N; conc. $ZnCl_2$, as in 57.

Exp. 59. Decomposition Voltage.   .

   Apparatus.—Coulometer cell; platinum electrodes; voltmeter and ammeter of low range; 2200-ohm rheostat; mercury to cover bottom of cell; connecting spiral of rubber-insulated copper wire.

   Results.—Almost theoretical.   Students are inclined to rush this experiment through and then to draw very poor curves.

Exp. 60. Ionic Displacement.

   Apparatus.—Outfit.

   Chemicals.—$SnCl_4$ sol., 5 per cent; sheet zinc in strips 1×2 cm.; iron wires No. 18, 30 cm. long; $SnCl_2$ sol., 5 per cent; $SbCl_3$ sol., 5 per cent; H_2S solution (take a 2-liter brown bottle, fill three-fourths full of water, add 10 cc. conc. NH_4HS sol., and *acidify* with HCl.—keep *corked*); strips of zinc, iron, and lead, 1×6 cm.; mercury.   (Do not let students put zinc in the clean mercury used in 59.)

   Results.—Perfect.

APPENDIX IV

Chemicals

The following list includes all the chemicals mentioned in Appendix III, arranged alphabetically.

(A) **Solutions and Liquids:**

Acetic acid N (57.1 cc. glacial acetic acid, sp. gr. 1.055 per liter).

Acetic acid, glacial.

Alcohol, absolute (not on the side shelf)

Alcohol, 96 per cent.

Aluminum chloride, 5 per cent.

Aluminum sulphate, 5 per cent.

Ammonium chloride, 5 per cent.

Ammonium hydroxide, conc., sp. gr. 0.90.

Ammonium hydroxide, N (66 cc. conc. NH_4OH, sp. gr. 0.90, per liter).

Ammonium thiocyanate, 5 per cent.

Antimony trichloride, 5 per cent.

Asbestos suspension (as in 13).

Barium chloride, 5 per cent.

Boric acid, 5 per cent.

Bromine water, conc.

Calcium chloride, 5 per cent.

Carbon tetrachloride.

Chromium sulphate, 5 per cent.

Congo red indicator, 1 per cent sol. in alcohol.

Cupric bromide (1 : $2\frac{1}{2}$).

Cupric sulphate, saturated.

Cupric sulphate, M/10 (25 gm. $CuSO_4 \cdot 5H_2O$ per liter).

Cupric sulphate N (125 gm. $CuSO_4 \cdot 5H_2O$ per liter).

Ether, U. S. P.

Ether, dried over sodium (not on the side shelf).

Ferric chloride, 5 per cent.

Ferrous sulphate, 5 per cent.

Hydrochloric acid, conc. sp. gr. 1.19.

Hydrochloric acid, 6N (dilute conc. with equal volume of water).

Hydrogen sulphide, saturated sol. (as in 60).

Iodine N/10 sol. in KI (12.7 gm. I_2, 25 gm. KI per liter).

Litmus, red (as in 41).

Litmus, blue (as in 41).

Magnesium sulphate, M/5 (49 gm. $MgSO_4 \cdot 7H_2O$ per liter).

Mercuric chloride, 5 per cent.

Mercuric nitrate, 5 per cent.

Mercury.

Methyl acetate, pure, anhydrous.

Methyl alcohol, pure, anhydrous.

Methyl orange, 0.1 per cent sol. in water.

Nitric acid, conc., sp. gr. 1.42.

Nitric acid, 6N (dilute 400 cc. conc. HNO_3, sp. gr. 1.42 to 1 liter).

Phenolphthalein, 1 per cent sol. in alcohol.

Phosphoric acid, M (68 cc. conc. acid, sp. gr. 1.7, per liter).

Potassium bromide, M/10 (12 gm. KBr per liter).

Potassium carbonate, 5 per cent.

Potassium chlorate, 5 per cent.

Potassium cyanide, 5 per cent.

Potassium dichromate, 5 per cent.

Potassium ferricyanide, 1 per cent (fresh).

Potassium iodide, 10 per cent.

Potassium nitrate, saturated sol.

Potassium ferric-oxalate (as in 29, must be fresh).

Potassium ferrocyanide, 5 per cent.

Propyl alcohol, pure, anhydrous (not on the side shelf).

Silver nitrate, test sol.

Silver nitrate, N/10 (17 gm. $AgNO_3$ per liter).

Silver nitrate, N/5 (34 gm. $AgNO_3$ per liter).

Sodium acetate, 5 per cent.

Sodium acetate N/5 (27.2 gm. $NaC_2H_3O_2 \cdot 3H_2O$ per liter).

Sodium chloride N/10 (5.8 gm. NaCl per liter).

Sodium chloride, 5 per cent.

Sodium hydroxide N/2 (standardized).

Sodium phosphate, di., 5 per cent.

Sodium sulphate, 5 per cent.

Stannic chloride, 5 per cent.

Stannous chloride, 5 per cent.

Succinic acid, M/10 (12 gm. $(CH_2COOH)_2$ per liter).

Sulphuric acid, conc., sp. gr. 1.84.

Sulphuric acid, 6 N (166 cc. conc. acid, sp. gr. 1.84, per liter).

Thymolphthalein, 1 per cent sol. in alcohol.

Zinc chloride, conc.
Zinc sulphate M/10 (29 gm. $ZnSO_4 \cdot 7H_2O$ per liter).
Zinc sulphate, N (144 gm. $ZnSO_4 \cdot 7H_2O$ per liter).

(B) **Solids:**

Agar-agar, powdered.
Aluminum wire, No. 12 (in 15-cm. lengths).
Ammonium chloride.
Ammonium oxalate.
Aniline sulphate.
Asbestos, long fiber.
Asbestos, for Gooch crucibles.
Brass wire gauze, 40-mesh (in pieces 2×4 cm.).
Cadmium nitrate.
Calcium chloride, anhydrous.
Cane sugar.
Copper turnings.
Cupric bromide.
Cupric oxide, wire form.
Cupric sulphate.
Ferric chloride.
Ferric oxide.
Ferric sulphate.
Ferrous ammonium sulphate.
Ferrous sulphide.
Gamboge.
Glass beads, 2 mm.
Iodine.
Iron, strips (1×6 cm.).
Iron wire, No. 18 (in 30-cm. lengths).
Lead strips (1×6 cm.).
Magnesium wire, No. 12 (in 15-cm. lengths).
Mercuric chloride.
Mercurous chloride.
Potassium bromate.
Potassium dichromate.
Potassium nitrate.
Potassium permanganate.
Salt, for refrigerating.
Silver nitrate.
Soda-lime, granulated.
Sodium.

Sodium acetate.
Sodium bicarbonate.
Sodium bromide.
Sodium carbonate (anhydrous).
Sodium chloride, pure, neutral.
Sodium hydroxide, pure by alcohol.
Sodium peroxide.
Sodium sulphate, anhydrous.
Sodium sulphate, decahydrate.
Sodium thiosulphate.
Starch, potato.
Tartaric acid.
Tin, granulated, 30-mesh.
Zinc, strips (1×6 cm.).

APPENDIX V

Apparatus

(A) **Student's Outfit.**—Each student is furnished with the following articles which he keeps during the year:

1 Air bath, graniteware.
6 Beakers, 2 each of 500, 300 and 100 cc.
5 Bottles, glass-stoppered, three 600 cc., two 1000 cc.
2 Bunsen burners.
2 Burettes, 1 Mohr, 1 stop-cock.
1 Büchner funnel, 9 cm.
1 Camel's hair brush.
2 Casseroles, 300 cc. and 125 cc.
2 Crucibles, No. 0 and No. 1, with covers.
1 Gooch crucible with disk.
1 Desiccator, 6-inch.
2 Evaporating dishes, 7 and 9 cm.
1 Filter stand.
1 Filter flask, 1 liter.
2 Flasks, graduated, 500 cc. and 1000 cc.
2 Flasks, Florence, 500 cc. and 1500 cc.
2 Flasks, Erlenmeyer, 250 and 500 cc.
4 Funnels, 6 cm., long stem.
1 Graduated cylinder, 50 cc.
1 Key for locker.
1 Mortar, 10-cm. porcelain, with pestle.
5 Pipettes, 1, 5, 10, 50, and 100 cc.
2 Ring stands, 2 clamps, and 1 four-inch iron ring.
1 Test-paper bottle.
6 Test-tubes, medium size.
1 Test-tube, 25×180 mm., heavy.
1 Tile, glazed porcelain, 6-inch.
1 Tongs, brass.
1 Transite board, 12×12 inch.
1 Tripod, iron.

1 Water bath, graniteware with 1 galvanized iron ring and 4 porcelain rings.*

2 Watch glasses, 7 and 10 cm.

1 Weighing bottle.

1 Waste jar.

(B) Non-returnable Articles:

The following articles are ordered from the storeroom as needed. They cannot be returned except in special cases which must be decided by the instructor:

Clay triangles	Rubber stoppers
Files	Rubber tubing
Filter paper	Sponges
Glass rods	Towels
Glass tubing	Test-tube brushes
Matches	Tube brushes
	Wire gauze

(C) Special Apparatus:

There are many other pieces of apparatus not included in the above lists. Most of these are a part of the common stock of any chemical laboratory. Any very special apparatus is either indicated in the sketches or is mentioned in the accompanying descriptions.

* A 3-quart graniteware stock pot with perpendicular sides used also as indicated in Exp. 11, etc. The iron ring serves as an adapter. It is turned over the edge of the pot and fits the largest porcelain ring.

APPENDIX VI

LOGARITHMS.

Natural Numbers	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS.

Natural Numbers.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
											PROPORTIONAL PARTS								
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7834	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	0996	0	1	1	2	2	3	3	3	4